PROCEEDINGS

OF

THE CHEMICAL SOCIETY.

Vol. XV. Nos. 202—216.

JANUARY—DECEMBER, 1899.

EDITED BY THE SECRETARIES.

LONDON:
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1900.

DATES OF ISSUE OF THE MONTHLY NUMBERS OF THE JOURNAL OF THE CHEMICAL SOCIETY TO FELLOWS.

January number	was issued	18th January.
February	„	18th February.
March	„	17th March.
April	„	13th April.
May	„	1st May.
June	„	1st June.
July	„	1st July.
August	„	1st August.
September	„	1st September.
October	„	1st October.
November	„	1st November.
December	„	1st December.

ERRATA.

Page.	Line.	
24	10	*for* "methylic-ψ-lauronolate" *read* "methyl ψ-lauronolate.
55	22	„ "camphor" *read* "camphene."
62	11	„ "propene" *read* "propane."
68	5	„ "bornylaminic" *read* "bornylamine."
71	14	„ "20°" *read* "21°."
77	8	*omit* "E. W."
239	23	*for* "acetaldehyde" *read* "acetic acid."

540.6 III C42 v. 15-17

LIST OF GRANTS MADE FROM THE RESEARCH FUND DURING THE YEAR.

£5 to W. A. Bone and J. J. Sudborough, to complete a research on the substituted succinic acids.

£10 to W. A. Bone, for an investigation of the cyanosuccinic esters.

£5 to F. S. Young, for an investigation of the products of the oxidation of benzene in presence of ferrous salts.

£20 to J. J. Dobbie, for an investigation of the decomposition products of corydaline.

£15 to A. Lapworth, for an investigation of the constitution of homocamphoronic and camphononic acids, and their relationship to camphoric acid.

£7 to J. A. Gardner, for an investigation of the constitution of camphopyric acid, and of its bromination products.

£20 to W. J. Pope, for an investigation of (a) the mechanism of the conversion of tertiary bases into quaternary ammonium derivatives; (b) the existence of an asymmetric nitrogen atom; and (c) the process of racemation.

£20 to A. W. Crossley and H. R. Le Sueur, to continue their research on the constitution of fatty acids.

£10 to R. S. Morrell and J. M. Crofts, to continue their research on the action of hydrogen peroxide on carbohydrates in the presence of ferrous salts.

£10 to F. W. Dootson, to continue his research on the condensation of methyl acetonetricarboxylate, the constitution of orcinoltricarboxylic acid, and the action of chlorine and bromine on the esters of acetonedicarboxylic acid.

£10 to J. J. Sudborough, to continue his research on the etherification constants of (a) normal fatty acids; (b) substituted acrylic acids; (c) ortho-substituted benzoic acids; and (d) substituted propionic acids, on diortho-substituted benzoic acids, and on the stereochemistry of unsaturated compounds.

£30 to W. J. Pope, to investigate (1) the arrangement in space of the groups attached to triad and pentad nitrogen; (2) to examine sulphonium compounds similarly; (3) to continue work on tetrahydroquinaldine and tetrahydro-β-naphthylamine; and (4) to extend the study of enantiomorphism.

£30 to H. E. W. Phillips, for an investigation of the constitution of phosphoric acid solutions by means of the electric conductivity methods of Kohlrausch.

LIST OF FELLOWS ELECTED DURING 1899.

Name.	Proposed.	Elected.
Aders, Robert Henry	April 20th	June 15th.
Allworthy, James Herbert	February 2nd	May 4th.
Allworthy, Samuel William, M.A.	December 1st, 1898	February 16th.
Anderson, James William	November 2nd	December 7th.
Armitage, Francis Paul	,, ,,	,, ,,
Armstrong, Frederick William	,, ,,	,, ,,
Atkinson, George Dekeyne	May 18th	June 15th.
Auchinachie, Peter	February 2nd	May 4th.
Baker, Clement Harrison	March 2nd	,, ,,
Beale, Frederick James	,, ,,	,, ,,
Bean, Percy	April 20th	June 15th.
Beasley, Frederic Arnold, B.Sc.	November 2nd	December 7th.
Belton, Frank	March 16th	May 4th.
Bennetts, Benjamin Harvey	,, ,,	,, ,,
Blackman, Walter Lionel	April 20th	June 15th.
Blackshaw, John Frank	December 1st, 1898	February 16th.
Blofeld, Stuart, B.A., B.Sc.	December 15th, 1898.	,, ,,
Bolam, Robert Alfred, M.D.	January 15th	,, ,,
Bond, Alfred Ernest	March 2nd	May 4th.
Bowles, Bertram H.	December 15th, 1898	February 16th.
Branscombe, William H., B.A.	November 17th, 1898	,, ,,
Bratby, George Smith	February 16th	May 4th.
Browning, Kendall Colin, B.A.	February 2nd	,, ,,
Carpenter, H. Cort H., B.A., Ph.D.	December 1st, 1898	February 16th.
Carpmael, Wilfred	April 20th	June 15th.
Chapman, Edgar Marsh	November 2nd	December 7th.
Cheater, Thomas John	December 15th, 1898	February 16th.
Collingridge, William, M.A.	February 2nd	May 4th.
Connah, James, B.Sc.	May 18th	June 15th.
Connell, Robert D.	March 16th	May 4th.
Cope, Frank	December 1st, 1898	February 16th.
Cozens, Thomas James	,, ,,	,, ,,
Danziger, Henry Meldola	May 4th	June 15th.
Darling, Charles Robert	March 2nd	May 4th.
Dewhirst, John Arthur	November 2nd	December 7th.
Dougall, James Dick	June 1st	,, ,,
Doyle, Frederick	April 20th	June 15th.
Dudderidge, Frank Rawlinson	November 2nd	December 7th.
Dunscombe, Frederick Charles	April 20th	June 15th.
Eichenauer, William Frederick	,, ,,	,, ,,
Epps, James Washington	January 15th	February 16th.
Estcourt, Harry Estcourt	November 17th, 1898	,, ,,
Fairweather, Ernest Barratt	January 15th	,, ,,
Farmer, H. F. F. Burdett	November 2nd	December 7th.
Fleischmann, F. N. Ashcroft	April 20th	June 15th.
Fraser, William Gordon	May 4th	,, ,,
Fry, George Cecil, B.Sc.	November 17th, 1898	February 16th.
Frye, Colin Charlwood	January 15th	,, ,,

Name.	Proposed.	Elected.
Gabriel, Edmund Vivian, M.A.	January 15th	February 16th.
Getman, Frederick Hutton	April 20th	June 15th.
Golding, John	November 17th, 1898.	February 16th.
Goltz, Harold Francis Carl	March 16th	May 4th.
Gurney, Elliott Henry	November 2nd	December 7th.
Haigh, Percy	March 2nd	May 4th.
Hall, Samuel Godfrey	December 1st, 1898	February 16th.
Harper, Henry Winston, M.D.	November 17th, 1898.	,, ,,
Hartley, Harold Brewer, B.A.	January 15th	,, ,,
Hedley, George Ward, M.A.	December 15th, 1898.	,, ,,
Hemborough, James	November 17th, 1898.	,, ,,
Henry, Thomas Anderson	December 1st, 1898	,, ,,
Hübner, Julius	April 20th	June 15th.
Hughes, John Elias	February 16th	May 4th.
Hunter, Archibald Glen Kidston	February 2nd	,, ,,
Johnson, Edward Charles	April 20th	June 15th.
Jones, Lauder William, A.B., Ph.D.	February 16th	May 4th.
Judge, Thomas, B.A.	March 2nd	,, ,,
Kay, Percy, Ph.D.	June 15th	December 7th.
Kinnersley, Henry Wulff	November 2nd	,, ,,
Knight, Harold Octavius	December 15th, 1898.	February 16th.
Lange, Ernest F. Stephen	June 1st	December 7th.
Laurie, Dudley Northall	December 15th, 1898.	February 16th.
Leeming, William Thomas, B.Sc.	November 2nd	December 7th.
Leon, Arthur Alexander	April 20th	June 15th.
Lett, Stephen Joshua	November 2nd	December 7th.
Lewis, Edward Watkin	,, ,,	,, ,,
Lindsey, Robert William	March 16th	May 4th.
Linstead, Edward Flatman	January 15th	February 16th.
Lucas, Alfred	November 17th, 1898	,, ,,
Luxton, Thomas, B.A., B.Sc.	December 1st, 1898	,, ,,
Mackenzie, Thomas	January 15th	,, ,,
MacLeod, James	March 16th	May 4th.
Main, Hugh, B.Sc.	June 15th	December 7th.
Martin, Samuel Montagu	November 17th, 1898	February 16th.
Mandsley, Joshua, B.A.	January 15th	,, ,,
McAlley, James	April 20th	June 15th.
McClumpha, Robert	May 18th	,, ,,
McConnel, William	March 2nd	May 4th.
McCracken, James	December 15th, 1898.	February 16th.
McCreath, William D.	November 2nd	December 7th.
Mirrlees, Arthur, B.A.	January 15th	February 16th.
Mohr, Bernhard, Ph.D.	,, ,,	,, ,,
Molson, John Cavendish	,, ,,	,, ,,
Morris, Wilfred Walter	March 2nd	May 4th.
Nance, John Trengrove, B.A.	January 15th	February 16th.
Neale, Harry Ainley	November 2nd	December 7th.
Nicholls, William W. Scott	January 15th	February 16th.
O'Sullivan, John	December 15th, 1898.	,, ,,

Name.	Proposed.	Elected.
Palmer, Thomas Henry	November 2nd	December 7th.
Panting, Laurence C., B.A., M.B.	February 2nd	May 4th.
Parkes, George Alfred	April 20th	June 15th.
Peachey, Stanley John	,, ,,	,, ,,
Pearson, Marchant, B.A.	November 2nd	December 7th.
Phillips, Eskricke Sidney, B.A.	May 18th	June 15th.
Pittuck, Frederick Williams	February 16th	May 4th.
Pixey, James Henry	November 17th, 1898	February 16th.
Polkinghorne, Bennett C., B.Sc.	November 2nd	December 7th.
Ponthieu, Georges	,, ,,	,, ,,
Price, Robert Coleman	November 17th, 1898	February 16th.
Pye, Frank J.	,, ,,	December 7th.
Pyne, Horace Seymour	January 15th	February 16th.
Raynor, William Downing, B.A.	November 2nd	December 7th.
Read, Harold McLean	February 16th	May 4th.
Roberts, James, jun.	December 1st, 1898	February 16th.
Rossiter, Sidney	April 20th	June 15th.
Roundell, Christopher Foulis, B.A.	November 2nd	December 7th.
Royal-Dawson, Henry	May 4th	June 15th.
Russell, William	November 2nd	December 7th.
Schryver, Samuel Barnet, D.Sc., Ph.D.	February 2nd	May 4th.
Schweich, Maurice Emile	March 2nd	,, ,,
Shelbourn, Edward Thomas	,, ,,	,, ,,
Shelton, Arthur John	February 2nd	,, ,,
Shepheard, William F. John	April 20th	June 15th.
Shepherd, John William, B.Sc.	May 18th	,, ,,
Simmons, Charles, B.Sc.	,, ,,	,, ,,
Skirrow, Frederick William, B.Sc.	December 1st, 1898	February 16th.
Soddy, Frederick, B.A.	November 17th, 1898	,, ,,
Stainer, John Ward	April 20th	June 15th.
Stansfield, Samuel, B.Sc.	May 4th	,, ,,
Stevenson, Arnold, B.A.	January 15th	February 16th.
Szarvasy, Charles Emerique, Ph.D.	December 1st, 1898	,, ,,
Thiersch, Harry Alexander	February 16th	May 4th.
Thomson, Robert Tatlock	February 2nd	,, ,,
Threlfall, Richard, M.A.	March 2nd	,, ,,
Tyler, Ernest Albert, B.A.	,, ,,	,, ,,
Wade, Arthur Luvian	February 16th	,, ,,
Walden, Allan Frederick, M.A.	March 16th	,, ,,
Walker, Charles	February 16th	,, ,,
Walter, Louis Heathcote, B.A.	November 17th, 1898	February 16th.
Walton, Robert Hawks	November 2nd	December 7th.
Watson, Fred Sheasby, B.Sc.	February 16th	May 4th.
West, George Hardstaff, B.Sc.	April 20th	June 15th.
White, Arthur Lee, B.Sc.	December 15th, 1898	February 16th.
White, Henry Fox	January 15th	,, ,,
Whittaker, Christopher Joseph	May 4th	June 15th.
Williams, William Arthur	November 17th, 1898	February 16th.
Wilson, F. R. Leyland, M.A.	November 2nd	December 7th.
Wilson, John	,, ,,	,, ,,
Wormell, Thomas Wilson, B.Sc.	December 1st, 1898	February 16th.

FELLOWS DECEASED.

Name.	Elected.	Died.
Buchanan, Joshua	May 4th, 1893	January 13th, 1899.
Bunsen, Robert Wilhelm	February 1st, 1842	August 16th, 1899.
Dey, Kanny Lall	June 17th, 1880	August 16th, 1899.
Dutta, Ramchandra	December 6th, 1883	January 17th, 1899.
Frankland, Sir Edward	December 20th, 1847	August 9th, 1899.
Friedel, Charles	May 18th, 1876	April 20th, 1899.
Galton, Sir Douglas	March 4th, 1875	March 10th, 1899.
Harkness, William	December 16th, 1875	September 5th, 1899.
Head, Jeremiah	March 16th, 1876	March 10th, 1899.
Hodges, John F.	April 15th, 1844	December 13th, 1899.
Jackson, Eric H.	December 5th, 1889	July 8th, 1899.
McDougall, Alexander	December 17th, 1857	November 13th, 1899.
Newton, Walter	March 4th, 1886	August 26th, 1899.
Nilson, L. F.	February 2nd, 1888	May 14th, 1899.
Ogston, G. H.	May 4th, 1871	July 19th, 1899.
Oxland, Robert	December 15th, 1851	May 11th, 1899.
Plimpton, R. T.	December 2nd, 1880	December 21st, 1899.
Rammelsberg, C. F.	May 3rd, 1866	December 29th, 1899.
Reynolds, Henry Charles	May 17th, 1888	May 1st, 1899.
Richardson, W. H.	November 17th, 1887	July 21st, 1899.
Stanford, Edward C. Cortis	April 21st, 1859	December 8th, 1899.
Sworn, Sidney Augustus	December 5th, 1889	May 10th, 1899.
Taylor, Andrew	December 2nd, 1875	
Tiemann, Ferdinand J. C. W.	March 17th, 1881	November 14th, 1899.
Watson, David	January 18th, 1872	December 15th, 1899.
Williams, W. Lloyd	February 15th, 1894	October 29th, 1899.

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3. Diortho-substituted benzoic acids. Part IV. Formation of salts from diortho-substituted benzoic acids and different organic bases. By Lorenzo L. Lloyd and John J. Sudborough	3	580
4. α-Ketotetrahydronaphthalene. By F. Stanley Kipping, D.Sc., F.R.S., and Alfred Hill	4	144
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6. Production of optically active mono- and di-alkyloxy-succinic acids from malic and tartaric acids. By Thomas Purdie, F.R.S., and William Pitkeathly, B.Sc.	6	153
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9. The thermal effects of dilution. By J. Holms Pollok, B.Sc.	8	—
10. Halogen derivatives of acetonedicarboxylic acid. Part I. By Frederick W. Dootson, M.A.	9	169
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12. Note on the interaction of formaldehyde with β-naphthylamine derivatives. By G. T. Morgan, B.Sc.	9	—
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14. On attempts to prepare pure starch derivatives through their nitrates. By Horace T. Brown, LL.D., F.R.S., and J. H. Millar	13	308
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16. Propylbenzenesulphonic acids. By Gerald T. Moody, D.Sc.	16	—

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27. A study of the absorption spectra of isatin, carbostyril, and their alkyl derivatives in relation to tautomerism. By W. N. Hartley, F.R.S., and James J. Dobbie, D.Sc., M.A.....	47	640
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44. Contribution to the characterisation of racemic compounds. By A. Ladenburg, For. Mem. C.S.	73	465
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58. Fencholenic acid. By G. B. Cockburn, B.A., B.Sc.	106	501
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61. The action of nitric oxide on nitrogen peroxide. By Harold B. Dixon and J. D. Peterkin	115	613
62. On the mode of burning of carbon. By Harold B. Dixon	118	680
63. Crystalline glycollic aldehyde. By Henry J. Horstman Fenton and Henry Jackson	119	575
64. On the blue salt of Fehling's solution and other cuprotartrates. By Orme Masson and B. D. Steele	120	725
65. The preparation of acid phenolic salts of dibasic acids. By S. B. Schryver, D.Sc., Ph.D.	121	661
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67. Scoparin. By Arthur George Perkin	123	—
68. On a new compound of arsenic and tellurium. By E. C. Szarvasy, Ph.D., and C. Messinger, Ph.D.	123	597

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77. On the relative efficiency of various forms of still-head for fractional distillation. By Sydney Young, D.Sc., F.R.S.	147	679
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86. Homocamphoronic and camphononic acids. By Arthur Lapworth and Edgar M. Chapman	159	980
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90. Methylisoamylsuccinic acid. I. By W. Trevor Lawrence	163	—
91. Condensations of anhydracetonebenzil and its analogues with aldehydes. By Francis R. Japp, F.R.S., and Alexander Findlay, M.A., B.Sc.	164	1017
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PROCEEDINGS

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January 19th, 1899. Professor Dewar, F.R.S., President, in the Chair.

Messrs. W. Ackroyd, E. M. Rich, and C. W. T. Woods were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Robert Alfred Bolam, 31, Oxford Street, Newcastle-on-Tyne; James Washington Epps, 95, Upper Tulse Hill, S.W.; Ernest Barratt Fairweather, King's College Hospital, Lincoln's Inn Fields, W.C.; Colin Charlwood Frye, Burwood, Woodville Road, Ealing, W.; Edmund Vivian Gabriel, Bengal United Service Club, Calcutta; Harold Brewer Hartley, Romney Lodge, New Park Road, Clapham Park, S.W.; Tom Lacey Hewitt, Beech Field, St. John's, Higher Broughton, Manchester; Edward Flaxman Linstead, 35, Hayter Road, Brixton Hill, S.W.; Thomas Mackenzie, 8, Gardner Street, Glasgow; Joshua Maudsley, Merchiston Castle, Edinburgh; Arthur Mirrlees, Redlands, Kelvinside, Glasgow; Bernhard Mohr, 69A Parliament Hill, Hampstead, N.W.; John Cavendish Molson, 42, Sackville Road, Hove, Brighton; John Trengove Nance, District Bank, Newcastle, Staffs.; William Walker Scott Nicholls, 230, Brockley Road, Brockley, S.E.; Horace Seymour Pyne, Castletown, Isle of Man; Arnold Stevenson, 4, Porchester Gardens, S.W.; Henry Fox White, Warnham, Woodland Road, Clifton, Bristol.

Of the following papers, those marked * were read:—

*1. "Researches on moorland waters. I. Acidity." By William Ackroyd, F.I.C.

Moorland waters are consumed by over five and a quarter millions of people in England. The quality of acidity possessed by these waters,

which has been associated with plumbo-solvent action, is therefore of great importance. The author differentiates between organic and inorganic acidity, and describes a method for ascertaining their amounts which consists of (1) titration with N/100 alkali, using phenolphthalein as indicator, and (2) aspiration of air free from carbon dioxide through another portion, and a second titration for the residual acidity. The precautions to be used are described.

Data are given showing the loss of acidity due to diffusion in observations extending over 181 days. Comparisons are made proving that the differences in acidity of waters from various gathering grounds are due to differences of gradient. It is finally shown that the organic acid in solution, always assumed to be humic acid, is of lower equivalent than that of the lowest humic acid known.

Discussion.

The President said that the plumbo-solvent action of the water supplied to Sheffield, Bradford, and Huddersfield, had been overcome by the addition of finely precipitated carbonate of lime in the reservoirs, with the result that the quality of the water was improved, not only by removal of the acidity, but also indirectly by precipitation of the dissolved peaty matter.

***2. "Esterification constants of substituted acetic acids." By John J. Sudborough and Lorenzo L. Lloyd.**

Goldschmidt has shown (*Ber.*, 1895, **28**, 3218) that the esterification of an organic acid in the presence of a catalytic agent, such as hydrogen chloride and of a considerable excess of alcohol, may be regarded as a monomolecular reaction, and may, therefore, be represented by the equation, $\frac{dx}{dt} = K(\quad - x)$, which, on integration, gives $K = \frac{1}{t} \log_e \frac{a}{a-x}$, where a is the initial concentration of the acid, $a - x$ the concentration of the acid after time t, and K the esterification constant. According to Goldschmidt, and also according to experiments made by the authors, K is directly proportional to the amount of hydrogen chloride present when dilute solutions are employed. In all cases K is calculated for normal hydrogen chloride.

The authors suggest that the letter E be used for the esterification constant, as K is already employed to denote the dissociation constant of an acid. E would then represent the esterification constant of an acid when normal hydrogen chloride is used, and $E^{10^\circ}_{EtOH}$ would represent the esterification constant of an acid with ethylic alcohol and a normal solution of hydrogen chloride at a temperature of 10°.

In the authors' experiments, N/40 hydrogen chloride was employed, and the organic acid was practically N/10 in all cases. Equal volumes of N/5 solutions of the acid in 100 per cent. ethylic alcohol, and of N/20 hydrogen chloride in 100 per cent. alcohol, were mixed, and 30 c.c. of the mixture run into small, stoppered bottles, and maintained at a temperature of 14·5°. The contents of these bottles were then titrated with N/10, and finally with N/20 alkali, phenolphthalein being employed as indicator. The constants were calculated from the equation, and the results are given in the following table, together with the dissociation constants where known.

Acid.	Formula.	$E\,^{14\cdot5^\circ}_{\mathrm{EtOH}}$.	K.
Acetic	$CH_3\cdot CO_2H$	3·661	0·00180
Propionic	$CH_2Me\cdot CO_2H$	3·049	0·00134
Chloracetic	$CH_2Cl\cdot CO_2H$	2·432	0·155
Phenylacetic	$CH_2Ph\cdot CO_2H$	2·068	
Bromacetic	$CH_2Br\cdot CO_2H$	1·994	0·138
Iodacetic	$CH_2I\cdot CO_2H$	1·713	0·075
Isobutyric	$CHMe_2\cdot CO_2H$	1·0196	0·00144
Trimethylacetic	$CMe_3\cdot CO_2H$	0·0909	0·000978
Dichloracetic	$CHCl_2\cdot CO_2H$	0·0640	5·14
Diphenylacetic	$CHPh_2\cdot CO_2H$	0·05586	
Dibromacetic	$CHBr_2\cdot CO_2H$	0·0510	
Trichloracetic	$CCl_3\cdot CO_2H$	0·0372	121·0
α-Bromisobutyric	$CMe_2Br\cdot CO_2H$	0·0356	
αα-Dibromopropionic	$CMeBr_2\cdot CO_2H$	0·0242	3·3
Tribromacetic	$CBr_3\cdot CO_2H$	0·01345	

It thus appears that the rate of esterification depends on the constitution of the acid rather than on its strength. The authors are engaged in determining the esterification constants of substituted acrylic acids, and hope to extend the work to other series.

***3. "Diortho-substituted benzoic acids. Part IV. Formation of salts from diortho-substituted benzoic acids and different organic bases." By Lorenzo L. Lloyd and John J. Sudborough.**

In continuation of their work on diortho-substituted benzoic acids (*Trans.*, 1895, **67**, 588 and 601; 1897, **71**, 229), the authors have attempted to prepare salts from 2 : 4 : 6-trinitrobenzoic, 2 : 4 : 6-tribromobenzoic, 2 : 4 : 6-tribromo-3-aminobenzoic, metanitrobenzoic, and benzoic acids, and the following bases: trimethylamine, tripropylamine, tribenzylamine, diethylaniline, aniline, metabromaniline, metanitraniline, 2 : 4- and 2 : 6-dibromaniline, pseudocumidine, mesidine, diphenylamine, and α- and β-naphthylamines, with results which are described in the paper. The investigation was undertaken in order

to determine whether the capacity to form salts is dependent on (1) the strength of the acid and of the base, or (2) the constitution of the acid and of the base, or on both of these.

It was thought probable that a tertiary base of high molecular weight might not be able to combine with a diortho-substituted acid, but the reverse has proved to be the case. Bases such as tribenzylamine, metanitraniline, &c., which will not combine with benzoic acid, readily combine with such diortho-substituted derivatives as 2 : 4 : 6-trinitrobenzoic, 2 : 4 : 6-tribromobenzoic, and 2 : 4 : 6-tribromo-3-aminobenzoic acids. This behaviour can only be accounted for by the fact that these are much stronger acids than benzoic, and combination between substituted benzoic acids and different bases would, therefore, appear to depend entirely on the strength of acid and strength of base.

Combination could not be effected between benzoic acid and metabromaniline, diethylaniline, pseudocumidine, or tribenzylamine, between metanitrobenzoic acid and tribenzylamine, and between trinitrobenzoic or tribromaminobenzoic acids and 2 : 4- or 2 : 6-dibromaniline, or diphenylamine.

The salts of trinitrobenzoic acid have no well-defined melting points; when heated, they become dark coloured, then melt and decompose, the temperature at which this occurs depending on the mode of heating. Most of the other salts have well-defined melting points.

***4. "α-Ketotetrahydronaphthalene." By F. Stanley Kipping, D.Sc., F.R.S., and Alfred Hill.**

The reaction involved in the synthesis of α-hydrindone from phenylpropionic chloride by means of aluminium chloride (*Trans.*, 1894, 65, 480) is probably capable of wide application, and the authors have commenced experiments recently with the object of studying its usefulness in various directions. It has been found that when phenylbutyric chloride is treated with aluminium chloride under suitable conditions, it is converted into α-ketotetrahydronaphthalene by intramolecular condensation, $C_6H_5\cdot CH_2\cdot CH_2\cdot CH_2\cdot COCl = C_6H_4\begin{<}{CH_2\cdot CH_2}{CO\cdot CH_2}\end{>} + HCl$; a reaction which is exactly analogous to that by which α-hydrindone is prepared.

α-*Ketotetrahydronaphthalene* is a colourless, highly refractive liquid, having a slight odour, faintly recalling that of both camphor and peppermint. The *semicarbazone*, $C_{10}H_{10}{:}N\cdot NH\cdot CO\cdot NH_2$, crystallises from alcohol in yellow needles or prisms, melts and decomposes at 217—220°, and is sparingly soluble in cold alcohol; when heated with dilute hydrochloric acid, it is decomposed, the ketone being regenerated. The *phenylhydrazone*, $C_{10}H_{10}{:}N\cdot NHPh$, crystallises from methylic

alcohol in massive, transparent plates melting at 84—85°; it is readily soluble in most ordinary solvents and is very unstable in the air. The *parabromophenylhydrazone*, $C_{10}H_{10}:N\cdot NH\cdot C_6H_4Br$, separates from alcohol and other solvents in long, colourless prisms and melts at 117—118°; it is more stable than the hydrazone, but, like the latter, is decomposed by hot hydrochloric acid, the product being probably analogous to that obtained from the hydrazone of α-hydrindone in a similar manner. The *oxime*, $C_{10}H_{10}:N\cdot OH$, separates from cold methylic alcohol in very large, well-defined, rhomboidal crystals; it melts at 102·5—103·5°, and is readily soluble in most ordinary solvents, but insoluble, or nearly so, in water. When reduced with sodium amalgam in acetic acid solution, the oxime is converted into a base, which is doubtless identical with the tetrahydro-α-naphthylamine described by Bamberger and Bammann (*Ber.*, 1889, 22, 951).

***5. "A new method for preparing unsymmetrical dimethyl- and trimethyl-succinic acids." By William A. Bone.**

When ethylic sodiomalonate or ethylic sodiomethylmalonate is treated with ethylic α-bromisobutyrate in alcoholic solution, a mixture of ethylic salts of tricarboxylic acids is obtained. This, on hydrolysis with concentrated hydrochloric acid, yields a mixture of isomeric methyl derivatives of succinic and glutaric acids, in which, however, the glutaric acid very largely preponderates, the yield of the isomeric succinic acid being very small.

This is due to the fact that, in presence of the strongly alkaline solution, the ethylic α-bromisobutyrate readily loses hydrogen bromide, forming ethylic methacrylate, which then condenses with the ethylic malonate, or ethylic methylmalonate, according to the equation $(CO_2Et)_2CH_2 + CH_2:CMe\cdot CO_2Et = (CO_2Et)_2CH\cdot CH_2\cdot CHMe\cdot CO_2Et$, and the resulting ethereal salt, on hydrolysis with concentrated hydrochloric acid, yields a methyl derivative of glutaric acid.

The author has found that if the sodium derivative of ethylic cyanacetate, which is almost insoluble in alcohol, be heated with an alcoholic solution of ethylic α-bromisobutyrate, the latter apparently does not lose hydrogen bromide, forming ethylic methacrylate, but reacts quite normally with the ethylic sodiocyanacetate, according to the equation $(CO_2Et)(CN)CHNa + BrCMe_2\cdot CO_2Et = (CO_2Et)(CN)CH\cdot CMe_2\cdot CO_2Et + NaBr$, and a very good yield of unsymmetrical ethylic dimethylcyanosuccinate is obtained. This, on hydrolysis with concentrated hydrochloric acid, yields practically the theoretical quantity of an acid melting at 139—140°, the composition and properties of which are identical with those of unsymmetrical dimethylsuccinic acid.

Unsymmetrical ethylic dimethylcyanosuccinate contains a hydrogen

atom replaceable by sodium. The sodium compound, which is soluble in alcohol, readily reacts with methylic iodide, yielding ethylic trimethylcyanosuccinate, and this, on hydrolysis with concentrated hydrochloric acid, is converted into trimethylsuccinic acid.

By means of these reactions, unsymmetrical di-and tri-methylsuccinic acids can be readily prepared in quantity. It is probable, moreover, that any mono-, di-, or tri-alkyl derivative of succinic acid may be prepared by starting with ethylic cyanacetate, and working on the lines indicated, the author is, therefore, making a special study of these reactions.

6. "Production of optically active mono- and di-alkyloxysuccinic acids from malic and tartaric acids." By Thomas Purdie, F.R.S., and William Pitkeathly, B.Sc.

In continuation of a previous research (*Trans.*, 1898, 73, 287), the authors have made further observations on the production of the ethereal alkyloxysuccinates in the interaction of silver malate and alkyl iodides. Small quantities only of these compounds were formed in the cases examined. A similar abnormal reaction occurs between silver tartrate and isopropylic iodide, an active ethereal salt of di-isopropoxysuccinic acid being found in the product; other alkyl iodides no doubt act in the same manner, though probably to a smaller extent.

The alcoholic hydroxyl groups of ethylic malate and tartrate are readily and completely alkylated by ethylic iodide in the presence of silver oxide. Diethoxysuccinic acid, obtained by this method, is a crystalline, highly dextrorotatory compound. The observations made on the rotatory powers of this acid and its ethylic, barium, and sodium salts furnish an explanation of the apparently anomalous results obtained by Rodger and Brame in preparing the alkylic tartrates from the silver salt (*Trans.*, 1898, 73, 301).

The method of alkylation by means of alkyl iodides and silver oxide, which does not appear to have been used previously, is generally applicable to the ethereal salts of hydroxy-acids, and probably also to other substances of a similar nature. As racemisation does not occur in the process, it is specially adapted for the preparation of optically active compounds.

7. "The action of ammonia on ethereal salts of organic acids." By Siegfried Ruhemann.

This paper is a continuation of the author's researches on the formation of pyridine derivatives from unsaturated acids. The ethylic salts of these acids have been prepared by the interaction of sodium ethoxide with a mixture of the salts of the acids of the malonic series

and those containing an acetylene linkage. Ethylic phenylpropene-tricarboxylate, on treatment with ammonia, is converted into *ethylic γ-phenyl-aa'-dihydroxy-β-carboxylate*, crystallising in colourless prisms melting at 200°, and *phenyldihydroxypyridine*, $CPh\langle\begin{matrix}CH\cdot C(OH)\\CH:C(OH)\end{matrix}\rangle N$, melting at 254—255°. Ethylic phenylbenzylglutaconate has been prepared from the product of the interaction of ethylic benzylmalonate and ethylic phenylpropiolate; on treatment with ammonia, it yields *γ-phenyl-β-benzyl-aa'-dihydroxypyridine* melting at 175°.

The author, further, gives an account of some experiments undertaken with the view of examining the action of ammonia on ethylic salts of saturated polycarboxylic acids. Ethylic propanetetracarboxylate is transformed into the diamido-imide of the acid (Ruhemann and Cunnington, *Trans.*, 1898, 73, 1006), but its homologue, ethylic β-methylpropanetetracarboxylate, forms the tetramide. Ethylic propanepentacarboxylate yields the triamido-imide of the acid, $NH\langle\begin{matrix}CO—CH—CONH_2\\CO—CH—CH(CONH_2)_2\end{matrix}$, melting at 212°, but ethylic phenylpropanetricarboxylate is transformed into the triamide melting at 230° with evolution of gas.

The author has also examined the action of sodium ethoxide on a mixture of ethylic phenylpropiolate with ethylic acetoacetate on the one hand, and with ethylic benzoylacetate on the other, and shows that the α-pyrone compounds, represented by the formulæ I and II, are formed respectively.

$CO_2Et\cdot C\langle\begin{matrix}CPh:CH\\CMe—O\end{matrix}\rangle CO$ I. M. p. 104°.

$CO_2Et\cdot C\langle\begin{matrix}CPh:CH\\CPh—O\end{matrix}\rangle CO$ II. M. p. 120—121°.

The action of ammonia on the first of these compounds has been studied; it does not lead to the formation of a pyridine derivative, but yields the ammonium salt, $NH_2\cdot CMe:C(CO_2Et)\cdot CPh:CH\cdot CO_2NH_4$, which regenerates the pyrone compound on treatment with acids.

8. "The changes of volume due to dilution of aqueous solutions." By E. B. H. Wade, B.A.

In this paper, the contraction of solutions of different substances at various concentrations has been studied experimentally. Contraction is defined as the diminution of volume on mixing equal volumes of water and solution, stated for 100,000 c.c. of resulting solution; *e.g.*, if 50 c.c. of water + 50 c.c. of solution yield 99·999 c.c. of diluted solution, the contraction is said to be unity. Concentration is defined as the number of gram equivalents of substance in every 100,000 c.c. of the solution after dilution.

The author describes an apparatus for measuring such contractions directly to within about one-tenth of a unit without the need of determining the specific gravities of the experimental liquids. Observations were made on solutions of hydrogen, sodium, potassium, calcium, and strontium chlorides, potassium ferrocyanide, oxalic acid, cane-sugar, and urea. In almost all cases the equation $X = \frac{n^b}{a}$ was found to hold good in which X is contraction, n concentration, and a, b are constant terms. In such cases Φ, the apparent volume of the substance, must be given by $\Phi = \text{const.} + \frac{n^b - 1}{a(2^b - 1)}$, and values of Φ thus calculated for various values of n are tabulated in the paper.

The first equation shows how X varies with the concentration. If the concentration be kept constant, and the dissolved substance varied, it is found that X increases regularly with the equivalent weight of the dissolved substance.

The apparatus described is available for many other cases where a change of volume follows a chemical process, as in the neutralisation of an acid.

9. "The thermal effects of dilution." By J. Holms Pollok, B.Sc.

In thermo-chemical determinations, it is customary to operate with very dilute solutions to simplify the calculations connected therewith. To determine how far dilution might affect the thermal condition of salts in solution, a number of saturated solutions of salts were diluted with an equal bulk of water, and the following changes of temperature were noted.

Saturated solutions at 9°.	Thermal change on dilution.		Saturated solutions at 9°.	Thermal change on dilution.	
	1st Expt.	2nd Expt.		1st Expt.	2nd Expt.
$NaCl$	+0·50	+0·50	$(NH_4)_2SO_4$	−0·43	−0·39
$NaNO_3$	−1·80	−1·85	$CaCl_2$	+0·58	+0·62
Na_2SO_4	−0·05	−0·03	$BaCl_2$	−0·07	−0·06
Na_2CO_3	−0·15	−0·20	$MgSO_4$	+0·02	−0·01
KCl	−0·47	−0·47	$ZnSO_4$	+0·03	+0·05
KNO_3	−0·32	−0·38	$CuSO_4$	+0·02	+0·05
K_2SO_4	−0·04	−0·03	$FeSO_4$	+0·04	+0·00
K_2CO_3	−0·37	−0·44	$Pb(NO_3)_2$	−0·37	−0·33
NH_4Cl	−0·15	−0·13			

The method employed was as follows: saturated solutions of the various salts were made, and half a litre of each placed in

glass bottles of that capacity; an equal number of bottles were filled with half a litre each of distilled water, then all were placed in a large, shallow, wooden tub in a room of uniform temperature, and left for 24 hours. A number of thin glass beakers of about a litre capacity, with glass stirring rods shaped into a ring at the end, were provided, also a mercury thermometer graduated into tenths of a degree, and reading easily to a quarter of each division, as well as a differential alcohol thermometer with only about 4° on the whole stem, and the graduations of which corresponded to less than 0·01°. The temperatures of the bottles were taken as the experiments were made and were found to be almost exactly 9°, though the different bottles did in point of fact vary as much as 0·05°, for which a proper correction was made. A bottle of solution and a bottle of water were then lifted out of the bath by a piece of flannel and poured simultaneously into a beaker standing on a thick piece of flannel, stirred up, and the temperature noted by both thermometers.

10. "Halogen derivatives of acetonedicarboxylic acid. Part I." By Frederick W. Dootson, M.A.

This communication is a preliminary note of an investigation of the action of halogens on ethylic acetonedicarboxylate. By the action of dry chlorine, *ethylic tetrachloracetonedicarboxylate* has been obtained. This substance, after purification, is a colourless, crystalline compound which melts at 30—30·5°, and decomposes on hydrolysis with aqueous soda or potash. It reacts with alcoholic potash, forming dichloromalonic and dichloracetic acids, and with ammonia yielding the amides of these acids. The action of bromine is very similar to that of chlorine.

11. "The detection and determination of sucrose in the presence of lactose." By Edwin Dowzard.

The method proposed by the author is based on the fact that sucrose is inverted by citric acid, whilst lactose is unaffected. The rotatory power of a solution of lactose is determined before and after treatment with citric acid. If the lactose is pure, the rotation remains unchanged, but if sucrose is present it is considerably decreased. The amount of sucrose is readily calculated from the decrease in rotation.

12. "Note on the interaction of formaldehyde with β-naphthylamine derivatives." By G. T. Morgan, B.Sc.

With a view of explaining the interactions which occur between formaldehyde and β-naphthylamine (*Trans.*, 1898, 73, 536), the author has investigated the action of this reagent on alkyl, benzyl, and halogen derivatives of the base.

Dibenzyl-β-naphthylamine, $C_{10}H_7N(CH_2Ph)_2$, crystallises from alcohol in colourless leaflets, and from ethylic acetate in clusters of hard, transparent prisms; it melts at 119—120°.

One compound only results when formaldehyde reacts with dialkyl- and dibenzyl-β-naphthylamine, two molecular proportions of the base condensing with one of the aldehyde to form a dinaphthylmethane derivative. The following compounds have been obtained: *tetramethyl-ββ-diaminodinaphthylmethane*, $CH_2(C_{10}H_6NMe_2)_2$, which crystallises in transparent, colourless prisms melting at 144°, the *tetrethyl* derivative, $CH_2(C_{10}H_6NEt_2)_2$, which crystallises in large, colourless prisms and melts at 114°, and the *tetrabenzyl* derivative, $CH_2[C_{10}H_6N\cdot(CH_2Ph)_2]_2$, which forms lustrous leaflets melting at 164°.

The formation of these derivatives seems to be due to substitution in the contiguous α-position, as compounds of a different type are formed with methylene in the side chain when a halogen atom occupies this α-position.

Methylene 1-bromo-2-naphthylamine, $C_{10}H_6BrN{:}CH_2$, is obtained when 1-bromo-2-naphthylamine is treated with formaldehyde in acetic acid or in alcoholic solution; it crystallises from benzene or chloroform in colourless needles, and melts, with decomposition, at 144—145°. The corresponding *chloro*-derivative, $C_{10}H_6Cl\cdot N{:}CH_2$, obtained from 1-chloro-2-naphthylamine, crystallises in colourless needles and melts at 179—180°. Both substances are compounds of the anhydroformaldehyde type, and are converted into their generators on hydrolysis with acids, whilst the dinaphthylmethane bases are not altered under these conditions.

The investigation is being extended to other derivatives of β-naphthylamine.

At the next meeting, on Thursday, February 2nd, 1899, the following papers will be communicated:—

"Maltodextrin, its oxidation products and constitution." By H. T. Brown, LL.D., F.R.S., and J. H. Millar.

"On attempts to prepare pure starch derivatives through their nitrates." By H. T. Brown, LL.D., F.R.S., and J. H. Millar.

"An isomeride of amarine." By H. Lloyd Snape, D.Sc., Ph.D., and Arthur Brooke, Ph.D.

"Propylbenzenesulphonic acids." By G. T. Moody, D.Sc.

"The chemistry of the so-called nitrogen iodide. Parts I.—VII." By F. D. Chattaway, M.A., K. S. P. Orton, M.A., and H. P. Stevens, B.A.

"Derivatives of dibenzylmesitylene." By W. H. Mills and T. H. Easterfield.

"The action of chlorosulphonic acid on the paraffins and other hydrocarbons." By Sydney Young, D.Sc., F.R.S.

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February 2nd, 1899. Professor Dewar, F.R.S., President, in the Chair.

Mr. F. W. Dootson was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. James Herbert Allworthy, Laxton School, Oundle; Peter Auchinachie, 12, Mid Street, Keith, N.B.; Kendall Colin Browning, St. John's College, Cambridge; William Collingridge, Port Sanitary Office, Greenwich, S.E.; Archibald Glen Kidston Hunter, Dunedin, New Zealand; Lawrence Christopher Panting, 9, Beverley Road, Anerley, S.E.; Samuel Barnett Schryver, D.Sc., Ph.D., 27, Arundel Gardens, W.; Arthur John Shelton, 19, Sturry Street, Poplar, E.; Robert Tatlock Thomson, 156, Bath Street, Glasgow.

Of the following papers, those marked * were read:—

***13. "Maltodextrin, its oxidation products and constitution." By Horace T. Brown, LL.D. F.R.S., and J. H. Millar.**

The subject of this paper is the maltodextrin which occurs amongst the intermediate products of starch hydrolysis with diastase, and to which the empirical formula $\begin{cases} C_{12}H_{22}O_{11} \\ (C_{12}H_{20}O_{10})_2 \end{cases}$ has hitherto been assigned (Brown and Morris, *Trans.*, 1885, 47, 527). Although present in considerable quantities in starch-transformations which have been arrested at the right point, its preparation in a pure state, and in sufficient amount for extended work, is a very laborious process. When isolated, it was found to have properties corresponding to $[\alpha]_D$ 181—183, and R 42—43, and was completely hydrolysed to maltose by diastase, and to *d*-glucose by acids.

When maltodextrin is carefully oxidised with mercuric oxide and barium hydroxide until its power of reducing Fehling's solution disappears, the greater part of the product is obtained as the barium salt of a definite and complex carboxylic acid, which is provisionally called *maltodextrinic acid A*. This has been isolated. Its properties correspond to $[\alpha]_D$ 192·3, R 0, and its calcium salt contains 2·4 per cent. of calcium. Maltodextrinic acid A is hydrolysed both by diastase and by dilute acids. Under the action of diastase, it yields 40 per cent. of maltose, and 60 per cent. of another carboxylic acid of less complexity; this is *maltodextrinic acid B*, the calcium salt of which contains 3·8 per cent. of calcium.

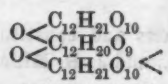
When hydrolysed by dilute oxalic acid, maltodextrinic acid A yields 85·8 per cent. of *d*-glucose, and another still simpler acid which is shown to be a C_5-derivative. Maltodextrinic acid B, when hydrolysed by oxalic acid, also yields this same C_5-acid and 67·7 per cent. of glucose.

The final C_5-acid corresponds in composition to $C_5H_{10}O_6$, and appears to be a normal carboxylic acid derived from a pentose. Since this acid can now be prepared in fair quantities by the oxidation of maltose with mercuric oxide, the authors expect to be able very soon to put its exact nature beyond doubt. It has many properties in common with those of xylonic acid.

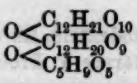
If the constitutional formula of maltose is taken as

$$CH_2OH\cdot CHOH\cdot CH\cdot(CHOH)_2\cdot CH\cdot O\cdot CH_2\cdot(CHOH)_4\cdot CHO,$$
$$\qquad\qquad\qquad\qquad\quad \backslash\!\!-\!\!O\!\!-\!\!/$$

the polysaccharide maltodextrin may be regarded as being made up of three such molecules with the elimination of the elements of $2H_2O$. Written in an abbreviated form, the formulæ of maltodextrin and of maltodextrinic acid A may be expressed thus:



Maltodextrin.

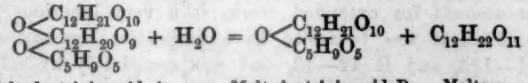


Maltodextrinic acid A.

the sign $<$ being used to denote the open carbonyl.

The hydrolysis of maltodextrinic acid A in two successive steps by diastase and acids respectively may be represented in the following manner.

(1) *Diastase hydrolysis.*



Maltodextrinic acid A. Maltodextrinic acid B. Maltose.

(2) *Acid hydrolysis.*

$$O\begin{matrix}C_{12}H_{21}O_{10}\\C_5H_9O_5\end{matrix} + 2H_2O = C_5H_{10}O_6 + 2C_6H_{12}O_6$$

Maltodextrinic acid B. Pentose acid. Glucose.

In an appendix to the paper, the authors describe the standard methods they now employ to determine the amount of glucose which a carbohydrate or its derivative yields on complete hydrolysis with oxalic acid. The results of thus hydrolysing soluble starch, maltose, maltodextrin, and maltobionic acid are given.

***14. "On attempts to prepare pure starch derivatives through their nitrates." By Horace T. Brown, LL.D., F.R.S., and J. H. Millar.**

This paper records the efforts made by the authors to obtain some of the hydrolytic products of starch in a pure state by preparing their nitric esters and regenerating them by treatment with ammonium sulphide.

Although perfectly successful as regards soluble starch, it was not found possible to regenerate from their nitrates substances like maltodextrin, amylodextrin, and the stable dextrin, the recovered product always showing signs of having undergone some oxidation during the nitration process. All the reducing starch-products, *i.e.*, those with an open carbonyl group, yield on nitration and regeneration indeterminate mixtures containing carboxylic acids.

***15. "The stable dextrin of starch transformations, and its relation to maltodextrin and to soluble starch." By Horace T. Brown, LL.D., F.R.S., and J. H. Millar.**

When starch is transformed by an active diastase, such as that derived from an air-dried malt, at temperatures below 60°, the reaction proceeds with great rapidity until a resting stage is reached corresponding to $[\alpha]_D$ 150, R 80, for the mixed products of change. At this stage, these products consist of maltose, and a dextrin which, comparatively speaking, is very resistant to the further action of the hydrolytic agent. An account is given of the mode of separation, and the dextrin was obtained ultimately with optical and reducing properties corresponding to $[\alpha]_D$ 195—195·7, and R 5·7 to 5·9. This residual reducing power is a property inherent to the dextrin, and is not due to admixture with a second reducing substance. This was shown by oxidising the dextrin with mercuric oxide and baryta, a definite dextrinic acid being produced.

Dextrinic acid is a complex carboxylic acid with distinct but feeble acid properties. It forms a well-defined calcium salt, containing

0·31 per cent. of calcium, and under the influence of acid hydrolysis yields *d*-glucose and a residual C_6-acid, which is shown to be identical with that obtained by the complete acid hydrolysis of the two maltodextrinic acids already described. The amount of glucose given by this hydrolysis has been determined.

Dextrinic acid and its salts, and also the dextrin from which it is derived, unlike maltodextrin and maltodextrinic acid A, are but very slowly hydrolysed by diastase. After many hours' treatment at 50—60°, a certain limited amount of change takes place, the resulting products being maltose and glucose in about equal proportions. The glucose is not derived from previously formed maltose, since it is observed when a malt-extract absolutely devoid of any maltose-hydrolysing power is employed.

The available evidence all points to the conclusion that the stable dextrin and the derivative polysaccharide acid, dextrinic acid, are built up of C_6-, and not, as in the case of maltodextrin, of C_{12}-groups. The dextrin molecule may be empirically regarded as made up of 39 $C_6H_{10}O_5$ groups in combination with a terminal $C_6H_{12}O_6$ group; or, more correctly, as a condensation of 40 glucose molecules, with the elimination of $39H_2O$. All the known properties of these substances agree with the view that their constitution may be expressed by the formulæ:

$$O_{39}\begin{cases} C_6H_{11}O_5 \\ (C_6H_{10}O_4)_{38} \\ C_6H_{11}O_5 \end{cases}$$

Stable dextrin.

$$O_{39}\begin{cases} C_6H_{11}O_5 \\ (C_6H_{10}O_4)_{38} \\ C_5H_9O_5 \end{cases}$$

Dextrinic acid.

The paper concludes with a discussion of the constitution of the starch molecule in the light of this new work.

Discussion.

Dr. Armstrong expressed the opinion that the formulæ suggested by the authors conveyed an idea of instability scarcely in accordance with the behaviour of the compounds in question. He could not help thinking that their structure was such that the ordinarily active groups were in some way shielded from attack or rendered unapproachable. Obviously, however, much more had to be learnt on such subjects. The complexity of the starch molecule was altogether remarkable when it was seen that in plants the formation of starch took place with extraordinary facility, and apparently under very simple conditions: thus starch could be detected in Spirogyra, originally depleted of the carbohydrate, after a very few minutes' exposure to light. It was most important to obtain further information on such a matter, as well as on the structure of the starch

molecule; he was glad, therefore, that Dr. Brown was also studying the problem from the biological side.

Mr. C. F. Cross remarked that the production of a C_5-hydroxy-acid under the conditions of the authors' experiments would add another and comparatively simple transition from hexose to pentose derivatives, and further generalise the tendency to form C_5-products—of which lævulinic acid and furfural are typical examples, but contrasted with the present case by complete elimination of alcoholic OH-groups. It would be important to determine whether a C_7-derivative were actually synthesised or the one C-atom in question eliminated as a CO-derivative.

Dr. G. Harris Morris said that the authors' account of the action of diastase on the stable dextrin probably explained the contradictory statements which had been made by different observers as to the formation of dextrose from maltose under the action of the enzymes of germinated and ungerminated cereals. In working with pure maltose and the cold-water extracts of several cereals, he had been unable to obtain the slightest evidence of any such action except in the case of maize, but others, using malt-extracts and starch-conversion products, had obtained indications of the formation of dextrose. It had been assumed that this dextrose was formed by the hydrolysis of the maltose contained in the starch-conversion products, but it would now appear that it resulted from the action of the diastase on the stable dextrin, and that his conclusion that malt contained no enzyme capable of hydrolysing maltose was correct.

Mr. A. R. Ling, in commenting on the observation that the dextrinic acids were well characterised substances, thought it was unfortunate that neither they nor their derivatives were crystalline. This was, perhaps, rather remarkable in the case of the acid of lowest molecular weight. He was glad to hear that the authors had convinced themselves that the so-called stable dextrin was a cupric-reducing substance. Mr. Baker and he had submitted numerous preparations of this dextrin to dialysis and fractional precipitation with aqueous alcohol for several months, and had thus obtained a final product having approximately the same optical and reducing powers as that observed by the authors.

Mr. J. F. Briggs asked what was the relation between the stable dextrin of R 5·5 and the dextrin which Dr. Brown formerly obtained by purification by means of mercuric cyanide: the latter had practically no reducing power.

Mr. Fenton said that he was particularly interested in the C_5-acid described by the authors, as, in conjunction with Mr. Jackson, he hoped to prepare a similar acid from erythrose by the hydrogen cyanide reaction.

Dr. BROWN, in reply, stated that the constitution of these reducing polysaccharides can perhaps be explained in the simplest way by regarding them as complexes built up much in the same manner as the hexose residues of maltose. If the currently accepted explanation of the constitution of maltose ever requires modification, this must of course modify our views as to the exact mode of combination of the constituent groups of the polysaccharides.

The constitution of the C_5-acid is at present occupying the attention of the authors. He agreed with Dr. Morris that these observations will go far to reconcile the conflicting statements with regard to the formation of dextrose from starch by diastase.

The non-reducing dextrins obtained in the older experiments by the mercuric cyanide method were no doubt maltodextrinic and dextrinic acids.

***16. "Propylbenzenesulphonic acids." By Gerald T. Moody, D.Sc.**

The results described in this note have been obtained in the course of an investigation on isomeric change (*Proc.*, 1888, **4**, 77; 1892, **8**, 90, 213, 214; 1895, 11, 48).

Propylbenzene readily sulphonates when shaken with one and a half times its own volume of ordinary sulphuric acid, and the product consists almost entirely of one propylbenzenesulphonic acid, the amide of which melts at 109—110°. This sulphonamide, on oxidation with potassium permanganate, yields 4-sulphonamidobenzoic acid (m. p. 280°), showing that it is derived from propylbenzene-4-sulphonic acid.

Propylbenzene-3-sulphonic acid and propylbenzene-2-sulphonic acid are obtained by reducing 2-bromopropylbenzene-5(13)-sulphonic acid and 4-bromopropylbenzene-2-sulphonic acid respectively. Propylbenzene-3-sulphonamide melts at 57°. Propylbenzene-2-sulphonamide yields 2-sulphonamidobenzoic acid ("saccharin," m. p. 222°) on oxidation with permanganate, and melts at 128°. This melting point is identical with that of the sulphonamide of the second acid obtained in small quantity on direct sulphonation, and is much higher than either that recorded by R. Meyer, or that by Claus for the sulphonamide obtained by them respectively from the acid which they consider to be propylbenzene-2-sulphonic acid, and regard as one of the products of direct sulphonation. It is to be noted, however, that these authors do not appear to have taken the precaution of purifying the hydrocarbon employed by them, and it is extremely likely that the fuming acid used gave rise to disulphonic acid.

Propylbenzene-3-sulphonic acid and propylbenzene-2-sulphonic acid do not undergo isomeric change when heated for several hours at 150°. The stability of the latter acid, compared with that of ethylbenzene-

2-sulphonic acid, which is converted into ethylbenzene-4-sulphonic acid at the temperature of the water-bath, is remarkable, more particularly when considered in conjunction with the fact that propylbenzene-2-sulphonic acid is either not formed, or, if formed direct, is produced only in small quantity by the direct sulphonation of propylbenzene.

The author proposes next to investigate the products of sulphonation of isopropylbenzene, more particularly with reference to Claus' statement that the primary product is the parasulphonic acid, and that this is converted into ortho-derivative both on heating at the temperature of the water-bath and on allowing it to remain for 10 weeks in sulphuric acid solution.

***17. "The chemistry of the so-called nitrogen iodide."**

"Part I. The preparation and properties of nitrogen iodide."
By F. D. Chattaway and K. J. P. Orton.

Well-defined crystals of nitrogen iodide have been obtained by several new reactions. They are best produced by adding ammonia to a solution of potassium hypoiodite containing 0·02 gram-molecule per litre. The liquid, after remaining clear for about half a minute, slowly deposits glittering needles, which are copper-coloured by reflected and red by transmitted light. These crystals have a specific gravity of 3·5, are dichroic, and probably belong to the orthorhombic system.

"Part II. The action of reducing agents on nitrogen iodide."
By F. D. Chattaway and H. P. Stevens.

All ordinary reducing agents rapidly decompose nitrogen iodide being themselves oxidised, whilst hydrogen iodide and ammonia are formed. The quantity of reducing agent oxidised is found in every case to be exactly double the amount equivalent to the hydrogen iodide produced.

The results obtained by the use of sodium sulphite, sulphurous acid, arsenious oxide, antimonious oxide, stannous chloride, and hydrogen sulphide are given in the following table:

Amount of reducing agent oxidised	Na_2SO_3	H_2SO_3	As_2O_3	Sb_2O_3	$SnCl_2$	H_2S
Amount of hydriodic acid simultaneously produced.	HI	HI	2HI	2HI	HI	HI

The iodine contained in nitrogen iodide, therefore, behaves towards reducing agents like the chlorine contained in a hypochlorite and exerts twice its normal oxidising action.

"Part III. The composition of nitrogen iodide." By F. D. Chattaway.

Scarcely any of the numerous published analyses of nitrogen iodide agree, those of the same observer often differing widely. It is usually stated that a number of distinct compounds exist, but this statement is based entirely on these discordant results, and is unjustifiable, for in no case has the substance analysed been shown to be pure, and in no case has the reaction on which the analysis is based been thoroughly studied; two reactions, indeed, must always have occurred, one of which has been overlooked. A method of analysis has now been investigated, and the conditions necessary for a single reaction to take place determined. By means of this method, specimens prepared by every reaction known to yield nitrogen iodide have been analysed, weighed quantities of the dry substance being employed in all important cases.

It is thus proved that only one compound exists, and that this has a composition represented by the formula $N_2H_3I_3$. The molecular weight and the manner in which the atoms are linked together remain to be settled by further investigation.

"Part IV. The action of light on nitrogen iodide." By F. D. Chattaway and K. J. P. Orton.

Nitrogen iodide suspended in ammonia is decomposed both by sunlight and by artificial light, forming nitrogen and hydrogen iodide, the latter being neutralised by the ammonia, $N_2H_3I_3 = N_2 + 3HI$. At the same time, a very small quantity of the compound is hydrolysed, ammonia and ammonium hypoiodite being formed, $N_2H_3I_3 + 3H_2O = 2NH_3 + 3HOI$; $2NH_3 + 3HOI + NH_3 = 3NH_4OI$. The ammonium hypoiodite, being somewhat unstable, slowly changes into ammonium iodide and ammonium iodate, $3NH_4OI = 2NH_4I + NH_4IO_3$.

Similar actions take place when nitrogen iodide suspended in water is exposed to light, and further, the hypoiodous acid and a portion of the hydrogen iodide interact, with the result that nitrogen is evolved, and iodine, hydrogen iodide, and ammonium iodide are formed. Powdered iodine, when placed in ammonia and exposed to light, is partially converted into nitrogen iodide, which then reacts normally.

"Part V. The action of alkaline hydrates, of water, and of hydrogen peroxide on nitrogen iodide." By F. D. Chattaway and K. J. P. Orton.

Solutions of alkaline hydrates rapidly decompose nitrogen iodide, two reactions simultaneously occurring even when light is completely excluded.

The chief reaction is one of hydrolysis, ammonia and an alkaline

hypoiodite being produced. These hypoiodites, however, are unstable, and more or less rapidly change into iodides and iodates. The equations representing the action of potassium hydroxide, for example, are $N_2H_3I_3 + 3KOH = 2NH_3 + 3KOI = 2NH_3 + 2KI + KIO_3$. At the same time, a portion of the nitrogen iodide always breaks down exactly as under the influence of light (preceding abstract), yielding nitrogen and hydrogen iodide, which combines with the base forming the iodide. Solutions of ammonia or hydroxides of the alkaline earth metals act similarly.

Water causes an analogous decomposition, but in this case the hypoiodous acid formed in the hydrolysis decomposes the hydrogen iodide produced, liberating iodine. The action of water on nitrogen iodide is rendered more rapid by the presence of basic oxides, and of salts, such as iodides and carbonates, which can combine or react with the hypoiodous and hydriodic acids formed.

Hydrogen peroxide dissolved in a solution of potassium hydrate rapidly decomposes nitrogen iodide, ammonia, potassium iodide, and a trace of potassium iodate being produced, whilst oxygen mixed with a little nitrogen is evolved. The nitrogen iodide first reacts with the potash as if it alone were present, being hydrolysed to ammonia and potassium hypoiodite, but at the same time breaking down partially into nitrogen and hydrogen iodide. A very small quantity of the hypoiodite is transformed into iodide and iodate, but the greater part reacts with the hydrogen peroxide, liberating oxygen and being converted into iodide thus, $KOI + H_2O_2 = KI + O_2 + H_2O$. If a solution of hydrogen peroxide alone be added to nitrogen iodide, the water hydrolyses the compound and a similar action ensues, whilst iodine is set free by a further action of hydrogen peroxide on the hydrogen iodide remaining uncombined.

"Part VI. The action of acids on nitrogen iodide." By F. D. Chattaway and H. P. Stevens.

Dilute acids, when added to nitrogen iodide suspended in water, first induce hydrolysis of the compound, hypoiodous acid is liberated together with ammonia, which combines with the acid added, $N_2H_3I_3 + \text{acid} + 3H_2O = (2NH_3 + \text{acid}) + 3HOI$. The further action depends on the nature of the acid used. If acids be employed such as sulphuric, phosphoric, boric, or acetic, on which hypoiodous acid has no effect, a rapid change into hydrogen iodide and iodic acid occurs, the former being immediately oxidised by a portion of the latter and iodine liberated, $15HOI = 10HI + 5HIO_3 = 6I_2 + 6H_2O + 3HIO_3$. If, however, the acid used reacts with hypoiodous acid, decomposition occurs, the nature of the final products depending on the acid employed. With hydriodic acid, for example, iodine is liberated,

one half coming from the nitrogen iodide and one half from the acid, $HOI + HI = I_2 + H_2O$; with hydrochloric acid, iodine monochloride is produced, $HOI + HCl = ICl + H_2O$; whilst with hydrocyanic acid, cyanogen iodide is formed, $HOI + HNC = INC + H_2O$.

In addition to this main action, it is found that when any acid except hydriodic or hydrocyanic acid is added to nitrogen iodide, light being excluded, a variable amount, depending on the strength of the acid, &c., decomposes exactly as it does under the influence of light yielding nitrogen and hydrogen iodide; this hydrogen iodide then reacts with some of the hypoiodous acid formed in the hydrolysis, liberating iodine.

"Part VII. Theory of the formation and reactions of nitrogen iodide." By F. D. Chattaway and K. J. P. Orton.

In the formation of nitrogen iodide from iodine and aqueous ammonia, the iodine is first converted into equivalent quantities of ammonium iodide and ammonium hypoiodite, $I_2 + 2NH_4OH = NH_4I + NH_4OI + H_2O$; the greater part of the latter is then transformed into nitrogen iodide, which separates as a solid, $3NH_4OI = N_2H_3I_3 + NH_4OH + 2H_2O$, but a small portion always remains unchanged. With iodine monochloride, similar actions occur, ammonium chloride and hypoiodite being, however, the first products, $ICl + 2NH_4OH = NH_4Cl + NH_4OI + H_2O$. If a solution of sodium or potassium hypoiodite be treated with a solution of ammonia, a partial conversion into the ammonium salt precedes the deposition of nitrogen iodide, $KOI + NH_4OH = NH_4OI + KOH$. Solutions of ammonia kept in contact with nitrogen iodide are found to contain ammonium hypoiodite, the concentration increasing with the concentration of the ammonia and with the temperature. Nitrogen iodide is therefore formed from ammonium hypoiodite by a reversible action. This is found to be in accordance with the law of mass action if the concentration of the electrolytically dissociated ammonium hydroxide, NH_4OH, and not the total concentration of the ammonia, NH_3, be considered.

The experimental evidence so far seems to point to the conclusion that nitrogen iodide bears to ammonium hypoiodite a relation similar to that which the amide bears to the ammonium salt of an acid. The constitution of the compound, however, is still doubtful. The simplest explanation of its chemical behaviour is found in formulæ such as NH_3,NI_3 or NH_2I,NHI_2, which represent each iodine atom as monovalent and directly connected with nitrogen. It is certain that neither iodine nor hydrogen iodide is present in loose molecular combination such as occurs in periodides or acid iodides.

Discussion.

Dr. Armstrong pointed out that, from an indexer's point of view, it was most important not to multiply papers unduly, and expressed the opinion that the four papers submitted by Messrs. Chattaway and Orton should be entered under the one simple title, "Nitrogen Iodide"; only two entries would then be required, in place of eight, in the authors' index.

In view of Dr. Chattaway's explanation that the error in the analyses communicated in his previous paper was due to exposure to light, it was worth noting, perhaps, that chemists were not sufficiently careful in excluding light: for years past he had been in the habit of brominating benzenoid hydrocarbons in the photographic dark room, with the result that products were obtained which were entirely free from the irritating odour of benzyl derivatives, and might be taken into a drawing-room without hesitation.

Dr. Scott referred to the much larger yield obtained when the iodine employed was dissolved in a solution of potassium iodide, and asked whether the substance so prepared was free from potassium compounds, and, bearing in mind Bunsen's formula, NH_2,NI_3, for nitrogen iodide, whether it was not probable that some, or even the whole, of the NH_3 might be replaced by compounds such as KI, giving rise to substances such as KI,NI_3. He also pointed out that none of the reactions described by the authors accounted for the large quantity of iodine set free when nitrogen iodide was treated with water at a temperature of 50—60°, a process employed by Stas for the preparation of pure iodine in large quantity and with perfect safety.

The President remarked that Guyard had suggested the employment of nitrogen iodide as an actinometer, so that the decomposition in light had been observed already. This decomposition was interesting, as it led to the inference that the iodide was an endothermic substance.

Dr. Chattaway, in reply, said that a full reference to Guyard's work was given in the paper. The authors were of opinion that they had settled finally the composition of nitrogen iodide, because every analysis made subsequent to the recognition of the causes of error confirmed it. The whole behaviour of the substance was in complete accord with this composition, and every reaction could be interpreted quantitatively.

The authors' results explained completely Stas' process for the purification of iodine. When nitrogen iodide is decomposed by water, two reactions had been shown to occur simultaneously and to an approximately equal extent: a part hydrolysed forming hypoiodous acid and ammonia, a part decomposed into hydrogen iodide and

nitrogen, and the hydrogen iodide and hypoiodous acid interacted liberating 90—95 per cent. of the total iodine. Slight explosions, however, were always liable to occur, and the process consequently was dangerous. No evidence had been obtained of the existence of potassium compounds such as those suggested by Dr. Scott.

18. "An isomeride of amarine." By H. Lloyd Snape, D.Sc., Ph.D., and Arthur Brooke, Ph.D.

From the distillation products, and also from the mother liquors obtained by the action of ammonium cyanide upon benzaldehyde, the authors have isolated a new base isomeric with amarine and melting at 198°. It forms salts with 1 equivalent of acids, forms a silver derivative containing 1 atomic proportion of the metal, and by distillation yields lophine.

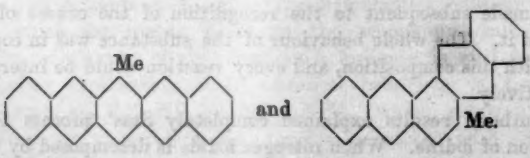
19. "The action of chlorosulphonic acid on paraffins and other hydrocarbons." By Sydney Young, D.Sc., F.R.S.

In a paper by Dr. F. E. Francis and the author (*Trans.*, 1898, 73, 932) it was shown that fuming nitric acid, at the temperature of a water-bath, acts far less energetically on normal paraffins than on iso-paraffins, methyl derivatives of the polymethylenes or aromatic hydrocarbons, and that, generally, the action is more rapid on hydrocarbons which contain a CH-group than on others.

Similar results have now been obtained with chlorosulphonic acid at the ordinary temperature, and it is shown that this reagent may be used for removing small quantities of isoparaffins and methyl derivatives of the polymethylenes from the normal paraffins separated from petroleum by fractional distillation.

20. "Derivatives of dibenzylmesitylene." By W. H. Mills and Thomas H. Easterfield.

With the object of synthesising hydrocarbons of the types



the authors have studied the benzoylation of mesitylene. Dibenzoylmesitylene has been described by Louise (*Ann. Chim. Phys.*, 1885, [vi], 6, 191), but its isolation is difficult under the conditions em-

ployed by him. A good yield of the compound is obtained, however, by the interaction of benzoyl chloride with mesitylene at low temperatures in presence of much aluminium chloride. It is readily reduced by zinc dust and alcoholic potash, forming dihydroxydibenzylmesitylene, $C_6HMe_3(CHPh\cdot OH)_2$, a thick oil boiling at 326—330° at 50 mm. pressure.

Dibenzylmesitylene is obtained from the secondary alcohol by prolonged reduction with zinc dust and alcoholic potash or, more conveniently, by boiling the diketone with hydriodic acid and phosphorus. Dibenzylmesitylene is sparingly soluble in cold, easily in hot alcohol, from which it crystallises in well-defined prisms. It melts at 89° and boils at 280° under a pressure of 30 mm. Its vapour density agrees with that required for the formula $C_{23}H_{24}$. This dibenzylmesitylene differs from that described by Louise (*loc. cit.*), which melted at 131° and was sparingly soluble in hot alcohol. It is not improbable that the latter is a tribenzylmesitylene, and, as analysis alone cannot settle this point, Louise's experiments are being repeated.

When dibenzoylmesitylene is oxidised in sealed tubes with dilute nitric acid at 140°, it is almost completely converted into two isomeric *dibenzoyluvitic acids*; a small quantity of *dibenzoylmesitylenic* acid is formed at the same time. The latter may be precipitated from a solution of the mixed sodium salts and sodium acetate by dilute acetic acid, and the uvitic acids from the mother liquor by hydrochloric acid. On treatment with methylic alcohol and hydrogen chloride, the crude dibenzoyluvitic acids yield two isomeric methylic salts. One of these is crystalline, melts at 248°, and is sparingly soluble in alcohol; the other is oily and easily soluble. On hydrolysis, the crystalline ethereal salt yields an acid melting at 262°; the isomeric acid from the oily salt melts at 210°. The acid of higher melting point is the more easily etherified.

The mixture of dibenzoyluvitic acids is oxidised by alkaline permanganate to a *dibenzoyltrimesic* acid, which crystallises from dilute hydrochloric acid in minute rosettes melting at 245°. Its salts, with the exception of the silver, copper, lead, and ferric compounds, are easily soluble.

The action of condensing agents on these compounds is being investigated.

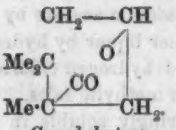
21. "On pseudocampholactone and pseudolauronolic acid." By Frederick H. Lees and W. H. Perkin, jun.

In a previous communication (*Proc.*, 1898, 14, 111), the authors showed that, when camphoric anhydride is treated in chloroform solution with aluminium chloride at ordinary temperature, there is formed,

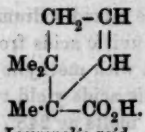
besides isolauronolic acid, a new lactone, $C_9H_{14}O_2$, isomeric with campholactone and named pseudocampholactone. On hydrolysing this with baryta, a syrupy acid, $C_9H_{16}O_3$, was obtained; this eventually solidified, and has been found to consist of two isomeric acids, $C_9H_{16}O_3$, melting respectively at 109° and 152°.

Pseudocampholactone readily interacts with phosphorus pentabromide, and on pouring the product into methylic alcohol, *methylic bromodihydro-ψ-lauronolate*, $C_8H_{14}Br{\cdot}CO_2Me$, is obtained; this boils at 160—165° at 35 mm., and when digested with diethylaniline yields *methylic-ψ-lauronolate*, which boils at 212—213° at 751 mm. pressure.

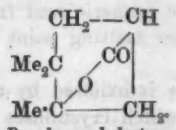
ψ-Lauronolic acid, $C_8H_{13}{\cdot}CO_2H$, obtained by hydrolysing its methylic salt, is a colourless oil boiling at 147—149° at 20 mm.; it is slightly lævorotatory and is an unsaturated acid, as its solution in sodium carbonate instantly reduces permanganate. On digestion with 33 per cent. sulphuric acid, it is converted into pseudocampholactone. This new acid is of special interest, because it is isomeric with lauronolic, isolauronolic, campholytic, and allocampholytic acids, and the authors consider it probable that the relationship between campholactone and lauronolic acid and pseudocampholactone and pseudolauronolic acid may be represented by the formulæ



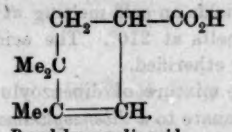
Campholactone.



Lauronolic acid.



Pseudocampholactone.



Pseudolauronolic acid.

Isolauronolic acid is not obtained when a solution of camphoric anhydride in chloroform is left in contact with aluminium chloride for several days, but in its place two new acids are formed: a crystalline saturated acid, $C_9H_{16}O_2$, melting at 76—77°, and a liquid unsaturated acid. These acids, as well as ψ-lauronolic acid, are being submitted to careful investigation, the results of which the authors hope soon to be able to communicate to the Society.

22. "Nitrocamphor as an example of dynamic isomerism." By T. Martin Lowry, B.Sc.

As has been pointed out in a previous communication (*Proc.*, 1898, 14, 152), the rotatory power of both nitrocamphor and π-bromonitrocamphor varies, not only when different solvents are used, but also with time, and this may be regarded as proof that the normal and pseudo-forms of these substances are isodynamic, the change of structure being attended with a change of rotatory power in the freshly-prepared solutions. The change of rotatory power of nitrocamphor has been studied in fifteen different solvents; it usually extends over a period of a few hours or days, but at higher temperatures, or in presence of a trace of piperidine or of sodium ethylate, takes place almost instantaneously; on the other hand, a solution in chloroform can often be kept in a labile state during several days, which is perhaps an indication that the change is due to the presence of some third substance. Equilibrium is reached in the case of both nitrocamphor and π-bromonitrocamphor when about 6 per cent. of the substance in solution is in the pseudo-form.

The author advances the opinion that the changes of rotatory power which take place in freshly-prepared solutions of many of the sugars are also due to the occurrence of isodynamic change, and not to the formation of hydrates, as has usually been assumed. In the case of glucose and of lactose, both isodynamic forms appear to have been isolated in an anhydrous state; when dissolved in water they pass to a condition of equilibrium in exactly the same manner as has been found to be the case with the isodynamic forms of π-bromonitrocamphor.

The bearing of the observations made with nitrocamphor on the general problem of dynamic isomerism is discussed in the concluding sections of the paper. The author hopes to extend this method of investigation to cyanocamphor and isonitrosocamphor, and to other optically active substances which may conceivably give rise to dynamic isomerides.

23. "Position-isomerism and optical activity; the methylic and ethylic salts of benzoyl- and of ortho-, meta-, and para-toluylmalic acid." By Percy Frankland, F.R.S., and Frederick Malcolm Wharton.

In continuation of their work on the influence of position-isomerism on optical activity, the authors have prepared and examined the following compounds. The rotation of each compound was determined at temperatures ranging from 20—137°. The results may be summarised as follows.

ethylic malate.		Ethylic malate.	
d 20°/4° = 1·2301	$[\alpha]_D^{20°} = -6·84°$	d 20°/4° = 1·1840	$[\alpha]_D^{20°} = -10·44°$
Methylic benzoylmalate.		**Ethylic benzoylmalate.**	
d 21°/4° = 1·2121	$[\alpha]_D^{21°} = -5·62°$	d 21°/4° = 1·1561	$[\alpha]_D^{21°} = -8·87°$
d 99°/4° = 1·1395	$[\alpha]_D^{99°} = -11·56°$	d 98°/4° = 1·0759	$[\alpha]_D^{98°} = -9·84°$
d 137·5°/4° = 1·1037	$[\alpha]_D^{137·5°} = -13·64°$	d 137°/4° = 1·0349	$[\alpha]_D^{137°} = -12·08°$
Methylic orthotoluylmalate.		**Ethylic orthotoluylmalate.**	
d 23°/4° = 1·1909	$[\alpha]_D = -8·91°$	d 21°/4° = 1·1391	$[\alpha]_D^{21°} = -6·25°$
d 98°/4° = 1·1161	$[\alpha]_D^{98°} = -12·40°$	d 100°/4° = 1·0714	$[\alpha]_D^{100°} = -10·38°$
d 135°/4° = 1·0822	$[\alpha]_D^{135°} = -14·09°$	d 136°/4° = 1·0405	$[\alpha]_D^{136°} = -12·01°$
Methylic metatoluylmalate.		**Ethylic metatoluylmalate.**	
d 20°/4° = 1·1925	$[\alpha]_D^{20°} = -6·34°$	d 21°/4° = 1·1371	$[\alpha]_D^{21°} = -4·67°$
d 99°/4° = 1·1127	$[\alpha]_D^{99°} = -11·73°$	d 99·5°/4° = 1·0603	$[\alpha]_D^{99·5°} = -9·93°$
d 136°/4° = 1·0753	$[\alpha]_D^{136°} = -13·49°$	d 137·5°/4° = 1·0229	$[\alpha]_D^{137·5°} = -11·66°$
Methylic paratoluylmalate.		**Ethylic paratoluylmalate.**	
d 18·5°/4° = 1·1957	$[\alpha]_D^{18·5°} = -8·14°$	d 20°/4° = 1·1382	$[\alpha]_D^{20°} = -0·22°$
d 99°/4° = 1·1088	$[\alpha]_D^{99°} = -8·33°$	d 99°/4° = 1·0513	$[\alpha]_D^{99°} = -5·55°$
d 136°/4° = 1·0688	$[\alpha]_D^{136°} = -10·14°$	d 136°/4° = 1·0106	$[\alpha]_D^{136°} = -7·31°$

Thus the lævorotation of ethylic malate is diminished by the introduction of all the acidyl groups in question. The lævorotation of methylic malate is also depressed by the introduction of the benzoyl, meta- and para-toluyl groups, but raised by that of the orthotoluyl group. At 20°, the depressing, or dextrorotatory, influence of the several groups follows in the order, para-toluyl>benzoyl>metatoluyl>orthotoluyl, both in the case of the methylic and ethylic compounds. At a high temperature (136°), on the other hand, the sequence of the dextrorotatory influences of these groups is paratoluyl>metatoluyl>benzoyl>orthotoluyl in the case of methylic malate, and paratoluyl>metatoluyl>orthotoluyl or benzoyl (practically identical) in the case of ethylic malate. In all cases, therefore, the dextrorotatory influence of the acidyl groups in question is more pronounced on the ethylic than on the methylic compound.

24. "Some regularities in the rotatory power of homologous series of optically active compounds." By Percy Frankland, F.R.S.

The author endeavours to explain the results obtained in the previous paper (Percy Frankland and Wharton) by adducing evidence that methylic and ethylic malates both exist as associated molecules, and that methylic is more associated than ethylic malate. It is suggested that the lower lævorotation of methylic as compared with

that of ethylic malate, is due to the greater degree of association of the former, and that, in the unassociated state, the lævorotation of the methylic salt would be the greater. The acidyl-malates are probably much less, if not entirely, unassociated, hence the invariably greater lævorotation of the methylic acidyl-malate as compared with that of the corresponding ethylic derivative. The author reviews a large number of other homologous series of optically active compounds, and investigates the degree of association of each term with the aid of Traube's method of calculating molecular volume. From this investigation, it would appear that the striking phenomenon of a maximum rotation occurring within an homologous series may probably be accounted for, in some cases, by the greater degree of association occurring in the initial terms, this association leading to the rotatory power actually observed being less than that possessed by the unassociated substance. In such cases, when a substitution is effected which does away with association, the maximum rotation within the series also disappears. Thus the malates exhibit a maximum rotation at the propylic term, whilst in the substituted malates the maximum disappears. In other cases, the existence of a well-defined maximum rotation within an homologous series would not appear to admit of explanation in this manner. Such maxima occur in all well-authenticated cases at about the butylic term of the homologous series, and the author suggests that this may be due to stereochemical causes, as the occurrence of some irregularity in the rotation might be anticipated at the point where a growing chain attached to the asymmetric carbon atom attains such a magnitude that the chain has doubled on itself, that is, when it contains about 5 carbon atoms. It is suggested that the same stereochemical cause may affect other physical properties, and that the greater tendency to association of the initial terms of an homologous series may be dependent on space conditions.

25. "On brasilin and hæmatoxylin." By A. W. Gilbody and W. H. Perkin, jun.

During the last three years, the authors have been investigating these important natural colouring matters, and now give a short abstract of the results obtained, in order that they may reserve the further study of the various decomposition products which they have prepared for the first time.

Trimethylbrasilin, $OH \cdot C_{16}H_{10}O(OMe)_3$, when oxidised under certain conditions with chromic acid, yields *trimethylbrasilone*, $OH \cdot C_{16}H_8O_2(OMe)_3$, which crystallises in straw-coloured needles, melts at 191°, and at a somewhat higher temperature loses $1H_2O$, forming *dehydrotrimethylbrasilone*, $OH \cdot C_{16}H_6O(OMe)_3$. This crys-

tallises in colourless needles, melts at 198°, and when treated with acetic anhydride is converted into an *acetyl* compound $OAc \cdot C_{16}H_6O(OMe)_3$, which melts at 176°, and is probably identical with the substance which Herzig (*Monats.*, 1895, 16, 913) obtained by oxidising acetyltrimethylbrasilin.

Nitric acid oxidises trimethylbrasilone, forming nitroparamethoxysalicylic acid (m. p. 232°) and a substance represented probably by the formula $C_{11}H_8O_5(OMe)_2$; the latter crystallises in yellow needles, yields an acetyl compound, reacts with phenylhydrazine and parabromophenylhydrazine, and is characterised by forming an intense purple solution in dilute alkalis. If this purple solution is gently warmed, decomposition sets in, with the production of paramethoxysalicylic acid (m. p. 157°) and two neutral substances, which melt at 118° and 206°, and which, on analysis, give numbers agreeing with those required for the formulæ $C_{11}H_{14}O_6$ and $C_{12}H_{14}O_6$ respectively.

From the mother liquors obtained during the preparation of trimethylbrasilone, the following substances have been isolated in small quantities. (*a*) A substance crystallising in colourless needles and melting at 183°. This has not yet been analysed. (*b*) A substance crystallising in colourless crystals, melting at 210°, and giving with ferric chloride an intense violet coloration; the analysis gave numbers agreeing with those required for the formula $C_9H_{10}O_5$. (*c*) A substance melting at 155°, which crystallises from water in colourless needles, and appears to be a lactone of the formula $C_{15}H_{16}O_6$. This lactone, on oxidation with permanganate, yields a dibasic acid, $C_{10}H_{10}O_3(CO_2H)_2$, which melts at 200—203° with decomposition, due to the formation of the anhydride. When this dibasic acid is heated with hydrochloric acid at 160°, it is decomposed with elimination of carbon dioxide, and on extracting the solution with ether, beautiful, colourless prisms are obtained, which melt at 104°, and consist of pure catechol; it thus appears probable that, in addition to the resorcinol ring, brasilin contains that of catechol.

When trimethylbrasilin is oxidised with permanganate, it yields an acid melting at 129·5°, which apparently has the constitution $C_{10}H_8O_3(OMe)(CO_2H)$, and which, on fusion with potash, gives an oil which shows all the characteristic reactions of resorcinol. This acid, on oxidation with sodium hypobromite, is converted into an acid represented probably by the formula $C_{10}H_{10}O_9$, and this, on further oxidation with permanganate, gives an acid, $C_8H_8O_6$, which melts at about 225° with decomposition.

When *tetramethylhæmatoxylin*, $OH \cdot C_{16}H_9O(OMe)_4$, is oxidised with chromic acid, it yields *tetramethylhæmatoxylone*, $OH \cdot C_{16}H_7O_2(OMe)_4$, which melts at about 170° with decomposition. When heated with acetic anhydride, it yields *acetyldehydrotetramethylhæmatoxylone*,

$OAc{\cdot}C_{16}H_5O(OMe)_4$, which crystallises in colourless needles, melts at 194°, and is probably identical with a compound melting at 191—192°, which Herzig (*loc. cit.*) obtained by oxidising acetyltetramethylhæmatoxylin.

When oxidised with nitric acid, tetramethylhæmatoxylone behaves in the same way as trimethylbrasilone, yielding a substance which crystallises in yellow needles, and dissolves in alkalis with a purple colour. This substance is being investigated, as also are several substances which have been obtained from the mother liquors obtained during the preparation of tetramethylhæmatoxylone. One of the latter compounds crystallises from water in colourless needles, melts at 214°, and on analysis gives numbers agreeing with those required for the formula $C_9H_{10}O_8(CO_2H)_2$.

The authors hope, by the examination of all these new substances, to obtain results which will enable them to assign formulæ to brasilin and hæmatoxylin, and they are continuing the investigation with the aid of Mr. H. Hibbert, B.Sc., who has already afforded much assistance in examining tetramethylhæmatoxylone.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Carnot, Adolphe. Traite d'Analyse des substances minerales. Tome premier, methodes generales d'analyse qualitative et quantitative. Pp. 992. Paris 1898. From the Author.

Deventer, C. M. van. Physical Chemistry for Beginners. Translated by R. A. Lehfeldt. Pp. xvi + 146. London 1898. From the Publisher.

Duffet, H. Recueil de Données Numeriques publié par la Société Francaise de Physique. Premier fascicule. Longueurs d'onde. Indices des Gaz et des Liquides. Pp. ix + 415. Paris 1898. From the Society.

Idris, T. H. W. Notes on Essential Oils, with special reference to their Composition, Chemistry, and Analysis. Pp. ix + 193. With Tables of Constants of the more commonly occurring Oils. London 1898. From the Author.

Kingzett, C. T., and Homfray, D. A Pocket Dictionary of Hygiene. Pp. 104. London 1898. From the Authors.

Salazar, A. E. Kalkulos sobre las Kanerias de Agua. Kon diagramas i tablas orijinales. Pp. xiv + 246. Santiago de Chile 1898. From the Author.

II. *Purchase.*

Effront, Jean. Les Enzymes et leurs applications. Pp. 370. Paris 1899.

Loew, Oscar. Die chemische Energie der lebenden Zellen. Pp. xi + 175. München 1899.

—— Ein naturliches System der Gift-Wirkungen. Pp. viii + 136. Munchen 1893.

Mitscherlich, Eilhard. Ueber das Benzin und die Verbindungen (1834). Herausgegeben von J. Wislicenus. Pp. 39. Leipzig 1898. (Ostwald's Klassiker der exakten Wissenschaften Nr. 98.)

Thorp, F. H. Outlines of Industrial Chemistry, a text-book for Students. Pp. xvii + 541. New York 1898.

Pamphlets.

Baker, R. T. On two new species of *Eucalyptus*. (From the *Proc.* Linnean Society, N.S.W., 1898.)

Mallet, J. W. On the claims of Davyum to recognition as a Chemical Element. (From *Amer. Chem. Journ.*, 1898.)

Mingaye, J. C. H. The Occurrence of Phosphatic Deposits in the Jenolan Caves, N.S.W.

—— Notes and Analyses of some N.S.W. Phosphatic Minerals and Phosphatic Deposits. (From the A. A. A. Sc., 1898.)

Raoult, F. M. Über Präzisionskryoskopie sowie einige Anwendungen derselben auf wässerige Lösungen. (From the *Zeit. für Physik. Chem.*, 27, 1898.)

Richards, T. W., and Lewis, G. N. Some Electrochemical and Thermochemical Relations of Zinc and Cadmium Amalgams. (From *Proc. Amer. Acad.*, 1898.)

Smith, H. G. On the Pinenes of the Oils of the genus *Eucalyptus*. Part I. (R.S.N.S.W., 1898.)

NOTICE TO AUTHORS.

As the *Proceedings* go to press on the Monday after each ordinary Meeting of the Society, the announcement of papers for the next Meeting cannot be made in this publication unless the papers are in the hands of the Secretaries by noon on that day.

At the next meeting, on Thursday, February 16th, 1899, there will be a ballot for the election of Fellows, and the following paper will be communicated by the author:—

"The absorption spectrum and constitution of cyanuric acid." By Professor W. N. Hartley, F.R.S.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

The following Candidates will be balloted for on Thursday, February 16th, 1899.

Allworthy, Samuel William,

The Manor House, Antrim Road, Belfast.

Medical profession, M.A., M.D., B.S., Trinity College, Dublin. Diploma in State Medicine and Scholarship in Experimental Science. Prizeman in Chemistry, &c.

A. Wynter Blyth.	*Robert Barklie.*
Hugh Woods.	*E. S. Cameron.*
Jos. F. Burnett.	*A. H. McConnell.*
Chas. R. C. Tichborne.	*T. Maxwell.*

Blackshaw, John Frank,

Holly Bank, Marton, Chelford, Cheshire.

Lecturer in Dairying and Assistant to the Professor of Agriculture, Glasgow and West of Scotland Technical College. Diploma in Agriculture, University College of North Wales. Special Diploma in advanced Agricultural Chemistry, University College of North Wales. National Diploma in Dairying, Royal Agricultural Society of England and Highland Agricultural Society of Scotland. Royal Agricultural Society of England Senior Examination, First Class. Highland and Agricultural Society of Scotland, do., First Class.

James J. Dobbie.	Edmund J. Mills.
Fred Marsden.	A. Humboldt Sexton.
G. G. Henderson.	Thomas S. Goodwin.

Blofeld, Stuart, B.A. (Lond.), B.Sc. (Lond.),

4, Camden Gardens, West Kensington Park, W.

Assistant Master in Science and Mathematics. Bachelor of Science of London University (one of the selected subjects being Chemistry). Science Master 7 years (in Chemistry especially) at (1) Teignmouth

Grammar School; and (2), Linton House School, Holland Park Avenue, W. Pupils have gained distinctions in Chemistry in University Local Examinations, and First Classes in S. K. Science and Art Examinations.

William Briggs.	*S. Barlet.*
J. Woodward.	*J. H. Robbins.*
Edwd. Jones.	*C. H. Burge.*

Bolam, Robert Alfred,
31, Oxford Street, Newcastle-on-Tyne.

Doctor in Medicine. Joint Lecturer in Physiological Chemistry, University of Durham College of Medicine, Newcastle-on-Tyne.

P. Phillips Bedson.	W. D. Halliburton.
F. C. Garrett.	Saville Shaw.

S. Hoare Collins.

Bowles, Bertram H.,
53, Dunsmure Road, Stamford Hill, London.

Manufacturing Chemist. Student for 3 years (Chemical Department) Technical College, Finsbury. Demonstrator's Assistant, Technical College, Finsbury. Experimental Chemist, Dartford Print and Dye Works. Works' Chemist at Shoreham Portland Cement Works. Works' Chemist, W. J. Bush & Co., Ltd., Manufacturing Chemists, Hackney.

R. Meldola.	Thomas H. Pope.
F. Southerden.	R. J. Friswell.
W. H. Barlow.	Geo. W. MacDonald.

Branscombe, William Harcourt,
Verona, Eastbourne.

Mining Engineer and Metallurgist. Graduate of Cambridge University (Sidney-Sussex College) in Applied Science. Passed in Assaying and Metallurgy (Part I.), Royal College of Science.

W. C. Roberts-Austen.	Alfred Stansfield.
Henry C. Jenkins.	Ernest A. Smith.

F. H. Neville.

Carpenter, Henry Cort Harold,
109, Banbury Road, Oxford.

Research Fellow in Chemistry in the Owens College, Manchester. Late Science Postmaster of Merton College, Oxford (1893—1896). B.A., first class in Final Honour School of Natural Science (Chemistry), Oxford. Ph.D. (Summa cum laude), University of

Leipsic (Saxony) (1896—1898). Dissertation: "Über eine Synthese des Tetraphenylcyclopentans," *Annalen*, 302, 223—236.

John Watts. V. H. Veley.
W. H. Perkin, jun. J. E. Marsh.
H. B. Dixon. W. Esson.

Cheater, Thomas John,

6, Boutflower Road, Wandsworth Common, S.W.

Analyst in the Government Laboratory. Student at Inland Revenue Laboratory and South Kensington (Royal College of Science), 1884—1885. Analyst in Government Laboratory since 1885. B.Sc. (London).

T. E. Thorpe. Edwd. Jones.
C. H. Burge. J. H. Robbins.
E. Grant Hooper. Geo. Stubbs.

Cope, Frank,

30, Leeds Road, Dewsbury.

Aniline Dye and Chemical Manufacturer. Engaged in the manufacture of dyes and drugs. Joint author with Mr. A. G. Perkin, F.R.S.E., on "Derivatives of Anthraquinone, Part III," and "The Constituents of *Artocarpus integrifolia*, Part I," Chemical Society's *Journal*.

J. J. Hummel. Herbert Ingle.
A. G. Perkin. Walter M. Gardner.
J. B. Cohen. Arthur Smithells.

Cozens, Thomas James,

The Grammar School, Middleton-in-Teesdale, Co. Durham.

Headmaster, the Grammar School, Middleton-in-Teesdale, part Examination for Licentiate Diploma (Honours Botany), College of Preceptors. Advanced Certificates, Science and Art Department, Agriculture, Hygiene and Botany, and Practical Chemistry. Certificates from Durham College of Science, Chemistry Practical and Theoretical, Botany Practical and Theoretical. Teacher of above subjects past 4 years.

H. D. Berridge. P. Phillips Bedson.
Alex. F. Hogg. *F. O. Solomon.*
F. C. Garrett.

Epps, James Washington,

95, Upper Tulse Hill, S.W.

Chemist in Chemical Manufactory. As a student spent 2 years at University and King's Colleges, London, and 2 years with Dr. Muter;

since then and at present engaged as a Chemist in the Analytica Laboratory and Works of Messrs. Allison of Hull.

John M. Thomson.	Herbert Jackson.
William Ramsay.	Morris W. Travers.
Patrick H. Kirkaldy.	John Muter.

A. H. M. Muter.

Estcourt, Harry Estcourt,

Hayesleigh, Old Trafford, Manchester.

Assistant Analyst, City Analyst's Laboratory, 20, Albert Square, Manchester. I have studied on the Science side at the Manchester Grammar School and attended classes at the Municipal Technical School. In the year 1890, I became a pupil in the Laboratory of the City Analyst of Manchester, and since then have had the opportunity of gaining a very varied experience in the analysis of all kinds of Food and Drugs, and commercial products. In 1895, I was Junior Assistant, with charge of pupils. I at present hold the position of Senior Assistant, and have control of the Laboratory in the absence of my uncle, Mr. Charles Estcourt.

C. Estcourt.	Francis Jones.
J. Carter Bell.	R. L. Taylor.
William Thomson.	*Jas. Grant.*

Fairweather, Ernest Barratt,

King's College Hospital, Lincoln's Inn Fields.

Head Pharmacist and Teacher of Practical Pharmacy in King's College Hospital. Studied Theoretical and Practical Chemistry and Physics under the late Mr. J. Woodland, F.C.S., and Mr. T. A. Ellwood, F.I.C. Is desirous of obtaining the Publications of the Society and consulting the Library.

John M. Thomson.	T. A. Ellwood.
Herbert Jackson.	Patrick H. Kirkaldy.
C. G. Moor.	*W. D. Halliburton.*

Fry, George Cecil,

1, Edinburgh Terrace, Newbury, Berks.

Science Teacher. Studied Chemistry in Yorkshire College, 1891—1896. B.Sc. (Vict.), Honours in Chemistry. Associate of the Institute of Chemistry. Science Master in Dronfield Grammar School, 1896—1897; in Newbury Grammar School, 1897.

Arthur Smithells.	A. E. Tutton.
Herbert Ingle.	C. F. Baker.
Julius B. Cohen.	*J. J. Hummel.*
Henry R. Procter.	*A. G. Perkin.*

Frye, Colin Charlwood,

Burwood, Woodville Road, Ealing.

Three years studying Chemistry at University College, London. Two years Demonstrator in Chemistry at the Pharmaceutical Society. Part author of "Note on the Action of Bromine on Benzene," *J. C. S.* Author of note on "Distilling Dilute Solutions of Potassium Permanganate with Sulphuric Acid in Vacuo," *Chem. News.*

J. Norman Collie. Arthur Lapworth.
William Ramsay. Morris W. Travers.
Thomas Tickle.

Gabriel, Edmund Vivian,

Bengal United Service Club, Calcutta.

Her Majesty's Indian Civil Service (Bengal). First Class Natural Sciences Tripos, Part I, and Second Class Natural Sciences Tripos, Part II, Cambridge University. Science Scholar of Emmanuel College, 1893—1898. Studying the subject of Agricultural Chemistry in India.

S. Ruhemann. R. S. Morrell.
M. M. Pattison Muir. J. Murray Crofts.
Francis Jones. *R. H. Adie.*
T. B. Wood. *W. T. N. Spivey.*

Golding, John,

1, Balmoral Road, Nottingham.

Agricultural Chemist, *i.e.*, Lecturer, Demonstrator, and Analyst to the Agricultural Department of the University College, Nottingham, under the County Councils of Notts, Derby, Leicester, and Lincoln (Lindsey Division). Chemical training in the Laboratories of the Pharmaceutical Society of Great Britain. Practical experience as Analyst and Lecturer: four years in R.A.S.E. Laboratory under Dr. J. A. Voelcker, one year under Essex County Council, and four years in present position. Original work, &c., published: *Journ. Soc. Chem. Ind.*, 16, 514, and 17, 125; *Transactions Nottingham Naturalists' Soc.*, 1896, 1897; *Midland Dairy Inst. Annual Reports*, &c.; and Board of Agriculture Report on "Distribution of Grants," &c. Work in hand, on Nitrogen Assimilation by Bacteria.

J. Augustus Voelcker. F. Stanley Kipping.
M. J. R. Dunstan. J. J. Sudborough.
R. M. Caven.

Hall, Samuel Godfrey,

19, Aberdeen Park, Highbury, N.

Soap Manufacturer. Studied Chemistry and Physics at University College, London, under Professors W. Ramsay and Carey Foster

during years 1893—1895; since then continued work in Laboratory of East London Soap Works, Bow, E.

William Ramsay.	John Spiller.
G. Carey Foster.	David Howard.
R. Meldola.	Thomas Tyrer.

Harper, Henry Winston, M.D.,
Austin, Texas, U.S.N.A.

Associate Professor of Chemistry, in charge of the School of Chemistry, and Director of the Chemical Laboratory of the (State) University of Texas. Studied at the Philadelphia College of Pharmacy, and afterwards at the University of Virginia (Medical Department) Formerly Chemist and Metallurgist to Colorado and Refugio Mining and Smelting Co. and Imogene Mining Co. in Mexico. Afterwards practioner of medicine, and for four years past in charge of School of Chemistry in the University of Texas. Author of published papers on *Rhus aromatica*, on solanin, on a deposit of magnesium sulphate in Brown Co., Texas, on some Texas waters, on certain toxicological cases, &c.

J. W. Mallet.	F. P. Venable.
F. P. Dunnington.	Jas. Lewis Howe.

W. L. Dudley.

Hartley, Harold Brewer,
Romney Lodge, New Park Road, Clapham Park, S.W.

Brackenbury Scholar in Natural Science, Balliol College, Oxford. Student of Chemistry.

John Conroy.	William E. Moss.
D. H. Nagel.	H. Brereton Baker.

A. Vernon Harcourt.

Hedley, George Ward,
2, St. Luke's Villas, Cheltenham.

Assistant Master, Cheltenham College. Open Exhibitioner in Natural Science, Merton College, Oxford, 1890—1894. 1st Class in the final School of Natural Science (Chemistry), 1894. M.A., 1897.

Francis Jones.	W. W. Fisher.
H. Brereton Baker.	William Esson.
John Watts.	J. E. Marsh.

Hembrough, James,
159, Hotwell Road, Clifton, Bristol,

Senior Lecturer in Chemistry, Leeds Southern Higher Grade School, Leeds. Ten years' scientific training, chiefly in Chemistry.

Honours in Practical Inorganic and Organic Chemistry, (S. and A. Dept.). Associate in Chemistry of the Royal College of Science, (Lond., 1894), Associate of the Institute of Chemistry (1897).

W. Palmer Wynne. Ernest H. Cook.
S. Parrish. T. E. Thorpe.
James Leicester.

Henry, Thomas Anderson,

37, Chelsea Gardens, S.W.

Assistant Chemist, Salters' Research Fellow in the Laboratories of the Imperial Institute. Student in the Pharmaceutical Society's School 1893—1894. Student in the Pharmaceutical Society's Research Laboratory, 1894—1896. Author, with Professor Dunstan, of the following papers: "A Chemical Investigation of the Constituents of Indian and American Podophyllum," *J.C.S.*, April, 1898; "The Volatile Constituents of *Goupia tomentosa*," *J.C.S.*, 1898. "Oxycannabin," *Proc., C.S.*, No. 189, 1898.

Wyndham R. Dunstan. C. M. Luxmoore.
H. A. D. Jowett. R. L. Jenks.
Ernest Goulding.

Hewitt, Tom Lacey,

Beech Field, St. John's, Higher Broughton, Manchester.

Student in Chemistry. Desirous of a Fellowship for Society's Publications, &c. Hold S. and A. certificates in Organic and Inorganic Chemistry, Advanced. For 8 months pupil under Mr. G. H. Hurst, F.C.S. For 6 months Junior Assistant Chemist at the Clayton Aniline Co. For 8 months Analyst to Mr. A. Hailwood, Milk Contractor, Manchester. Since October, 1897, Student at the Owens College. Member of the Society of Chemical Industry.

George H. Hurst. David Watson.
H. Grimshaw. Jas. R. Appleyard.
Thos. Southern, jun. *J. Lewkowitsch.*

Knight, Harold Octavius,

Westfield Villa, Barton-on-Humber.

Barytes and Whiting Manufacturer, &c. Student in the Chemical Laboratories of the Owens College, 1889—1891. Science Master, Wellington College, Salop, 1891—1896. Manufacturing Chemist since 1896.

Ernest Scott. H. B. Dixon.
Percy J. Winser. G. H. Bailey.
W. H. Perkin, jun.

Linstead, Edward Flatman,

35, Hayter Road, Brixton Hill, S.W.

Analytical Chemist. Chemist on the staff of Messrs. Burroughs, Wellcome and Co., London and Dartford.

Frederick B. Power.	Arthur R. Ling.
H. A. D. Jowett.	*B. E. R. Newlands.*

William J. Pope.

Lucas, Alfred,

Maison Hussein Pasha, Cairo, Egypt.

Analytical Chemist. Student Royal College of Science, South Kensington, London, 1891—1892. Analyst in the Government Laboratory, London, since 1892, now holding a temporary appointment under the Egyptian Government as Chemist to the Salt Department.

T. E. Thorpe.	C. Proctor.
E. Grant Hooper.	Edwd. Jones.
J. Woodward.	Geo. Stubbs.

Luxton, Thomas,

4, Cavendish Square, Margaret Street, Hull.

Teacher of Chemistry, Municipal Technical School, Hull. B.Sc. and B.A. (London). Have been engaged in teaching Chemistry and Physics entirely during the last 10 years. Formerly Science Master at Queen's College, Taunton, and at the Central Higher Grade School, Hull, and now head of Chemical Department, Technical School, Hull. Have at various times done Laboratory work in most branches of Chemistry and Chemical Physics.

John J. Pilley.	Harry Thompson.
Frederick William de Velling.	Fred. E. Johnson.
Alex. F. Hogg.	*H. Irving Foster.*

Mackenzie, Thomas,

8, Gardner Street, Glasgow.

Pharmaceutical Chemist. Teacher of Chemistry from March, 1895, in the Glasgow and West of Scotland School of Chemistry and Pharmacy. Major Examination of Pharmaceutical Society of Great Britain.

W. Watson Will.	*F. F. de Morgan.*
William Duncan.	*Peter MacEwan.*
W. L. Howie.	*R. R. Tatlock.*

W. Chas. Sayers.

Martin, Samuel Montagu,

Westwood, Princetown Road, Bangor, Co. Down.

Chemist, Analyst, and Chief of Laboratory of the firm of John

Clarke and Co., Limited, Manufacturing Chemists, Belfast. Licentiate of the Pharmaceutical Society of Ireland. Author of paper, "Pepsin and Essence of Rennett Chemically compared." Late Assistant Teacher of Chemistry, Belfast School of Applied Chemistry.

Bernard H. Paul. H. N. B. Richardson.
D. Lloyd Howard. *Lewis Ough.*
Thomas Tyrer. *R. E. S. Richardson.*

Maudsley, Joshua,

Merchiston Castle, Edinburgh.

Science Master. Hastings Exhibitioner in Chemistry and Physics, Queen's College, Oxford, 1892. First Class Honours in the Final School of Chemistry, Oxford, 1896. Science Master, Merchiston School, Edinburgh.

W. W. Fisher. V. H. Veley.
John Watts. J. E. Marsh.

H. L. Bowman.

McCracken, James,

580, Govan Road, Govan.

Manager and Secretary. Several years Analytical Chemist in Laboratory of Messrs. Wm. Beardmore and Co. and Wear Steel Co. For the past 7 years with the Carbon Cement Co., Limited, at present as Manager and Secretary. Technical Certificates in Honours Chemistry, Metallurgy, Mathematics, Theoretical Mechanics, Electricity and Magnetism, Iron and Steel Manufacture.

Edw. C. Stanford. Thomas S. Goodwin.
A. Humboldt Sexton. H. W. Dickinson.

G. G. Henderson.

Mirrlees, Arthur,

Redlands, Kelvinside, Glasgow.

Chemist to Sugar Factory, Sandwich Islands. B.A. (Chemistry) Cambridge.

J. Henry Gilbert. R. Haliburton Adie.
N. H. J. Miller. T. B. Wood.
John Bennet Lawes. R. S. Morrell.

Mohr, Bernhard,

69A, Parliament Hill, Hampstead, N.W.

Consulting Chemist. Ph.D. (Heidelberg).

Ludwig Mond. J. Wilson Swan.
Hugo Müller. W Kellner.

H. Sprengel.

Molson, John Cavendish, L.R.C.P., London.
42, Sackville Road, Hove, Brighton.

Physician and Surgeon. Fellow of the British Gynæcological Society, Fellow of the Royal Geographical Society, Member of the British Medical Association, formerly Student of Chemistry at the City and Guilds of London Institute, &c., &c.

Raphael Meldola. — Henry E. Armstrong.
Julian L. Baker. — *B. E. R. Newlands.*
A. M. Simpson. — *Arthur R. Ling.*
J. H. Coste.

Nance, John Trengove,
District Bank, Newcastle, Staff.

B.A., Oxford. Honours in Chemistry in Natural Science School, Oxford.

John Conroy. — William E. Moss.
D. H. Nagel. — R. Hornby.
A. Vernon Harcourt.

Nicholls, William Walter Scott,
230, Brockley Road, Brockley, S.E.

Assistant to Analysts in Government Laboratory. Student at Royal College of Science, Session 1891—1892. Demonstrator in Chemical Laboratory, Birkbeck Institution, Session 1887—1888, 1888—1889. Seven years' employment in Government Laboratory.

T. E. Thorpe. — E. Grant Hooper.
H. J. Helm. — J. Woodward.
C. H. Burge. — Edwd. Jones.

Northall-Laurie, Dudley,
56A, Pall Mall, S.W.

Student of the Institute of Chemistry of Great Britain and Ireland. Studying at King's College. Head of Cheltenham School in Chemistry, 1895. Student under Mr. Edgar Jackson, F.I.C., Analyst, 1896.

John M. Thomson. — J. H. Hichens.
Herbert Jackson. — *William Crookes.*
Patrick H. Kirkaldy. — *J. Augustus Voelcker.*

O'Sullivan, John,
742, Nicola Street, Vancouver City, B.C.

Chief Assayer and Chemist to the B.C. Agency, Limited, of London, England; 26 years' experience in practical assaying and Chemistry in Messrs. Vivian & Sons' Hafod Laboratory, Swansea. Obtained the following Certificates from Science and Art Department (London, England). 1st Class, E. and Lab. grant in Inorganic Chemistry 1876;

1st Class E. Metallurgy and 2nd Class Advanced Chemistry, 1st Class Advanced Theoretical and 2nd Advanced Practical, 1878.

W. Terrill. Clarence A. Seyler.
Christopher James. T. Rhymer Marshall.

Sydney W. Harris.

Pizey, James Henry,

9, Lady Somerset Road, Highgate Road, N.W.

Analytical Chemist. Studied one year in the Chemical Laboratories at University College, London; and three years in the Royal College of Science, of which half the time was devoted to Chemistry. I am now working in Laboratory of Mr. Blount, F.I.C., at Westminster.

William A. Tilden. M. O. Forster.
W. Palmer Wynne. Bertram Blount.
Chapman Jones. *W. Harry Stanger.*

Price, Robert Coleman,

Blacksburg, Virginia, U.S.N.A.

Professor of Chemistry in the Virginia Polytechnic Institute. Studied for three years at the University of Virginia, and for one year at Wiesbaden under the late Prof. Fresenius. For four years Assayist to the State Board of Agriculture of Virginia. For eight years Professor of Chemistry in the Virginia (State) Polytechnic Institute. Author of a paper on the composition and mineralogical relations of the mineral Tscheffkinite.

J. W. Mallet. F. P. Venables.
F. P. Dunnington. Jas. Lewis Howe.

Wm. L. Dudley.

Pyne, Horace Seymour,

Castletown, Isle of Man.

Lecturer in Science (Chemistry and Physics) at King William's College, Isle of Man. For 13 years Lecturer on Chemistry at King William's College, Isle of Man. Chemical Depolariser in conjunction with improved form of Primary Battery, Patent No. 15355, August 12th, 1893. Treatment of kelp with perchloride of iron for extraction of iodine.

Fred. H. Bowman. Francis Henry Tate.
T. A. Reid. *Edward Davies.*

Hy. Fairrie.

Roberts, James, jun.,

43, Great Western Road, Glasgow.

Chemist (Assistant to Professor of Chemistry). Commenced the study of Chemistry in the Glasgow and West of Scotland Technical College in 1893, proceeding from there to the Chemical Laboratory at

the University. Became an unofficial Assistant in Spring of 1896, and was appointed an official Assistant in May, 1897. Has engaged in research in the chemistry of coal, and is part author of several papers on the subject.

John Ferguson. Thomas Gray.
W. R. Lang. James Robson.
G. G. Henderson. *Matthew A. Parker.*
J. T. Bottomley.

Skirrow, Frederick William,
Graystongill, Bentham, Lancaster.

Student, B.Sc. (Vict.), First Class Honours in Chemistry, and Leblanc Medal for Applied Chemistry, Research Student in the Yorkshire College.

Arthur Smithells. J. B. Cohen.
H. R. Procter. Herbert Ingle.
John McCrae.

Soddy, Frederick,
Merton College, Oxford.

Student. Have been a Student of Chemistry since 1893, and obtained a First Class in the Final School in Chemistry, Oxford, 1898.

W. W. Fisher. John Conroy.
William Ramsay. D. H. Nagel.
John Watts.

Stevenson, Arnold,
4, Porchester Gardens, London, W.

Student, B.A. Cambridge, 1898. Educated at Winchester College, Clare College, Cambridge, 1893–1898. First Class Natural Science Tripos, Part I., 1897. Second Class Natural Science Tripos, Part II., 1898.

H. J. H. Fenton. W. J. Sell.
John M. Thomson. W. T. N. Spivey.
Thomas H. Easterfield. T. B. Wood.

Szarvasy, Dr. Charles Emerique,
19, Weymouth Street, Portland Place, W.

Research Chemist. Doctor of Philosophy. I have been four years student and four years as Lecturer at the University of Budapesth, one year worker at the University of Berlin, and at present worker at the Davy-Faraday Research Laboratory of the Royal Institution. Author of ten papers.

Alexander Scott. James H. Millar.
William Arbuckle. W. P. Bloxam.
Meyer Wilderman.

Walter, Louis Heathcote,

83, Holland Park Avenue, W.

Electrical Engineer and Engineering Chemist. B.A. Trin. Coll., Cambridge, Nat. Sci. Tripos, 1897. At present time assistant to Hiram S. Maxim, Esq., in his private laboratory.

M. M. Pattison Muir. Thomas Girtin.
R. S. Morrell. *S. Ruhemann.*
A. Hutchinson.

White, Arthur Lee,

29, Huron Road, Upper Tooting, S.W.

Student. B.Sc., (Lond.); Associate of the Institute of Chemistry; Associate of the Yorkshire College. Has worked four years at the Yorkshire College and two and a-half years at the Royal College of Science, London, where he is at present studying.

William A. Tilden. J. J. Hummel.
Arthur Smithells. W. Palmer Wynne.
Chapman Jones.

White, Henry Fox,

Warnham, Woodland Road, Clifton, Bristol.

Pharmaceutical Chemist. After Matriculation at London University in June, 1891, I was for three years a Student at Univ. College, Bristol, studying Chemistry under Dr. Young, F.R.S.. I then went to London, and for six months studied advanced chemistry (theoretical and analytical) under W. Watson Will, Esq., F.C.S., at the Metropolitan Coll. of Pharmacy. At the end of that course I passed the Major Examination of the Pharmaceutical Society. I have at present an engagement with Messrs. Giles, Schacht and Co. of Clifton as Manufacturing and Analytical Chemist.

Sydney Young. *F. Filmer De Morgan.*
W. Watson Will. *W. Chas. Sayers.*
Arthur Richardson. *Peter MacEwan.*
W. A. Shenstone.

Williams, William Arthur,

75, High Street, Wapping, London, E.

Chemist. Junior Demonstrator, City and Guilds Technical College, Finsbury, and Research Assistant to Professor R. Meldola, F.R.S., F.C.S., F.I.C.

R. Meldola. W. J. Dibdin.
Arthur J. Chapman. Robt. G. Grimwood.
R. Grimwood. J. H. Coste.

Wormell, Thomas Wilson,

184, Burrage Road, Plumstead, London, S.E.

Science Master and Lecturer at Woolwich Polytechnic. B.Sc. (Lond.); Final taken in Chemistry, Physics, and Mathematics. Honours 1st Class (S. Kensington) Practical Inorganic Chemistry. Teacher of Chemistry and Physics under Manchester School Board for two years, &c.

R. Lloyd Whiteley. Frank Clowes.

J. Bernard Coleman. J. J. Sudborough.

R. M. Caven.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

Issued 23/2/1899

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 15. No. 204.

February 16th, 1899. Professor Dewar, F.R.S., President, in the Chair.

Mr. W. S. Crouch was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. George Smith Bratby, Oak Field, Hale, Bowdon, Cheshire; John Elias Hughes, Birchville, Wrexham; Lauder William Jones, University of Chicago, Chicago, Ill., U.S.A.; Frederick William Pittuck, 19, Stratford Grove, Newcastle-on-Tyne; Harold McLean Read, 127, Warwick Road, Earl's Court, S.W.; Harry Alexander Thiersch, 8, Clifton Gardens, W.; Arthur Luvian Wade, 28, West Kensington Gardens, W.; Charles Walker, Scott Chambers, Pitt Street, Sydney, N.S.W.; Fred Sheasby Watson, Springside, Disley, Cheshire.

A ballot for the election of Fellows was held, and the following subsequently declared duly elected :—

Samuel William Allworthy, M.A.; John Frank Blackshaw; Stuart Blofeld, B.A., B.Sc.; Robert Alfred Bolam, M.D.; Bertram H. Bowles; William H. Branscombe, B.A.; H. Cort H. Carpenter, B.A., Ph.D.; Thomas John Cheater; Frank Cope; Thomas James Cozens; James Washington Epps; Harry Estcourt Estcourt; Ernest Barratt Fairweather; George Cecil Fry, B.Sc.; Colin Charlwood Frye; Edmund Vivian Gabriel, M.A.; John Golding; Samuel Godfrey Hall; Henry Winston Harper, M.D.; Harold Brewer Hartley, B.A.; George Ward Hedley, M.A.; James Hembrough; Thomas Anderson Henry; Harold Octavius Knight; Edward Flatman Linstead; Alfred Lucas; Thomas Luxton, B.A., B.Sc.; Thomas Mackenzie; Samuel Montagu Martin; Joshua Maudsley, B.A.; James McCracken; Arthur Mirrlees, B.A.; Bernhard Mohr, Ph.D.; John Cavendish Molson; John Trengove

Nance, B.A.; William Walter Scott Nicholls; Dudley Northall-Laurie; John O'Sullivan; James Henry Pizey; Robert Coleman Price; Horace Seymour Pyne; James Roberts, Jun.; Frederick William Skirrow, B.Sc.; Frederick Soddy, B.A.; Arnold Stevenson, B.A.; Charles Emerique Szarvasy, Ph.D.; Louis Heathcote Walter, B.A.; Arthur Lee White, B.Sc.; Henry Fox White; William Arthur Williams; Thomas Wilson Wormell, B.Sc.

The PRESIDENT announced that Mr. C. E. Groves, F.R.S., had resigned the Editorship of the Society's Journal, and that Dr. W. P. Wynne, F.R.S., had been appointed to succeed him. The Council had recorded their sense of Mr. Groves' services to the Society in a vote of thanks, a copy of which would be engrossed on vellum and presented to him at the Anniversary Meeting.

It was announced that the following changes in the Officers and Council were proposed by the Council:—

As *President*.—Professor T. E. Thorpe, Ph.D., D.Sc., LL.D., F.R.S., *vice* Professor James Dewar, M.A., LL.D., F.R.S.

As *Vice-Presidents*.—Mr. C. E. Groves, F.R.S., and Professor Thomas Purdie, Ph.D., F.R.S., *vice* Professor F. R. Japp, M.A., LL.D., F.R.S., and Professor W. A. Tilden, D.Sc., F.R.S.

As *Hon. Secretary*.—Dr. Alexander Scott, F.R.S., *vice* Dr. W. P. Wynne, F.R.S.

As *Hon. Treasurer*.—Professor W. A. Tilden, D.Sc., F.R.S., *vice* Professor T. E. Thorpe, LL.D., F.R.S.

As *Ordinary Members of Council*.—Mr. H. Brereton Baker, M.A., Professor F. Clowes, D.Sc., Dr. G. T. Moody, and Professor James Walker, D.Sc., *vice* Professor Bedson, D.Sc., Mr. Hehner, Professor McLeod, F.R.S., and Dr. Scott, F.R.S.

Dr. H. T. Brown, F.R.S., Dr. A. W. Crossley, and Mr. R. J. Friswell, were appointed to audit the Society's accounts.

Of the following papers, those marked * were read.

*26. "On the absorption spectrum and constitution attributed to cyanuric acid." By W. N. Hartley, F.R.S.

The spectrum of cyanuric acid was described by the author in 1882, (*Trans.*, 41, 84) as exhibiting an absorption band between wave-lengths 2747 and 2572, and the formula deduced was that of a symmetrical trihydroxybenzene in which the three CH-groups are replaced by three nitrogen atoms. The bulk of the original preparation having been carefully preserved, its absorption spectrum has been photographed again with the improvements and modifications devised by

the author in 1883 (*Phil. Trans.*, 1885, 176, 471). The results show that 2·5 grams of cyanuric acid, when dissolved in hot, distilled water, made up to 500 c.c. and placed in cells respectively 200 mm. and 100 mm. in length, exhibited nothing which could be described as an absorption band. In the first case, the warm solution cut off the spectrum sharply at about wave-length 2572, but transmitted the rays only weakly from about 3330, and in the 100 mm. cell the spectrum was cut off sharply at 2483. The spectra thus obtained are in complete harmony with the formula $(H{\cdot}N{:}C{:}O)_3$, but not with that formerly given.

A searching examination of all the conditions and circumstances surrounding the preparation of the solutions and photographs of the original spectra shows that the possibility of any foreign substance getting into the cyanuric acid was almost precluded. But as the specimen was purchased, there might have been, perhaps, a milligram or less of some solid substance adhering accidentally to the lip of the bottle, or attached to the cork, which would be weighed out with the first quantity of crystals. There are many well-known substances, of which a milligram would suffice to produce the effect observed.

***27. "A study of the absorption spectra of isatin, carbostyril, and their alkyl derivatives in relation to tautomerism." By W. N. Hartley, F.R.S., and James J. Dobbie, D.Sc., M.A.**

In this paper, the authors trace the relation between the curves of molecular absorption and the constitution of isatin, carbostyril, and their alkyl derivatives. They start from the fact (*Phil. Trans.*, 1879, 170, Part I, 257) that the substitution of a methyl or ethyl group for an atom of hydrogen without other alteration in the structure of the substance, merely increases the general absorption, *i.e.*, slightly shortens the transmitted spectrum without making any difference in the character of the absorption, and show that when the curves of molecular absorption of the substances studied are compared, a very close resemblance is seen to exist between the parent substance and one of the two isomeric derivatives.

In the carbostyril group, the spectra of carbostyril, methylcarbostyril, and methyl- and ethyl-pseudocarbostyril are compared. Carbostyril and methylpseudocarbostyril both show an absorption band in the same position, and the spectra of the two substances are, in other respects, almost identical, the only difference being that the general absorption is slightly increased in the case of methyl- and ethyl-pseudocarbostyril, which is the effect usually produced when alkyl radicles are substituted for hydrogen. The spectra of methylcarbostyril differ in a marked manner from those of carbostyril and methyl-

pseudocarbostyril; the absorption band occupies a different position, is less persistent and less intense than the corresponding band of the latter, and the amount of the general absorption is less.

Isatin and its derivatives show similar relations. In the spectra of isatin there are two absorption bands. The spectra of methylpseudoisatin closely resemble those of isatin, likewise exhibiting two absorption bands, and about the same extent of general absorption. In methylisatin, there is only one strong absorption band.

The authors conclude that the very close resemblance between the curves of molecular absorption of carbostyril and methyl- and ethylpseudocarbostyril and between those of isatin and methylpseudoisatin, point to identity of constitution, and, inasmuch as the chemical behaviour of methylpseudocarbostyril and methylpseudoisatin show that these compounds are lactams, the lactam constitution must also be assigned to carbostyril and isatin. This conclusion agrees with that arrived at by Goldschmidt and Meissler (*Ber.*, 1890, **23**, 253), who employed a purely chemical method in their investigations, and with the more recent results of Knorr (*Annalen*, 1896, **293**, 81).

A detailed account of the various spectra is given in the paper.

Discussion.

Dr. J. H. Gladstone said that the study of the selective absorption of the rays of light by different substances was a physical method of research which, in his opinion, had been too much neglected. It was capable, beyond doubt, of distinguishing between different compounds of an elementary substance, and, in some instances, of throwing light on their constitution. If the absorption of rays of light by a compound were always the sum of the absorption of its separate constituents, or if different compounds of the same element gave totally different spectra, this mode of analysis would be of little use: investigation showed, however, that similarity is often associated with suggestive differences. Thus, in the case of ferric salts, the extreme red ray is always transmitted with the greatest ease, whilst the blue-green and other more refrangible rays are soon absorbed; yet the rapidity of absorption varies very much, as may be seen in the great difference in the degree of redness of such ferric salts as the nitrate and sulphocyanide. Observations such as these were much facilitated by placing the liquid in a hollow prism instead of in a cell with parallel sides, as, in this way, the gradual absorption of the various rays by different thicknesses could be seen and mapped at once. The absorption of different kinds of rays might be employed for the purpose of chemical research, each having, no doubt, its own story to tell, and fruitful results might be expected from the use, not only of the

coloured rays of the visible spectrum and of the more refrangible rays which Professor Hartley is engaged in photographing, but also of the less refrangible heat rays, and even, perhaps, of the X rays in the future.

Professor DOBBIE pointed out that the relation of such substances as isatin and its methyl derivatives to one another had long been a vexed question, and that it had not been found possible to solve it by means of chemical methods. The advantage of the spectroscopic method was that the uncertainty, due to possible shifting of the atoms in the course of a chemical reaction, did not arise. It was interesting to note that the results obtained by this method were in complete agreement with those most recently arrived at by chemical processes, in which care had been taken to eliminate, as far as possible, the sources of error inseparable from the older methods.

Dr. A. HARDEN referred to Schiff's work on the isolation of tautomeric forms of ethylic acetoacetate, and asked whether experiments had been made with the object of isolating and of examining spectroscopically the enolic form of isatin.

The PRESIDENT said that every physical method which in any way could aid in establishing the identity of a material under investigation was of the utmost importance to future workers. A substance might seem to be pure so far as evidence derived from ordinary analytical methods was concerned, and yet reveal the presence of impurity when its ultra-violet spectrum was examined. This was the case with water, the ultra-violet spectrum of which was most characteristic, and served to indicate the presence of water vapour in gases dried by the ordinary methods. He was inclined to think that some improvement might be made in the selection of the material for obtaining the ultra violet spectrum. The cadmium spectrum was open to the objection that wide gaps existed in which no lines were present, and the use of a material such as iron, which gave a spectrum of lines more evenly distributed in the ultra-violet, would seem to be preferable.

Professor HARTLEY, in reply, said that, when working with rays of high refrangibility, it had been found best to use a quartz cell in which the faces were parallel.

The use of the iron spectrum for the study of absorption spectra had attracted his attention in the past, and was referred to in the paper published in 1879; the objections to its use were that too many lines were present, and that two very strong groups existed in the more refrangible part where absorption bands were likely to occur. The best electrodes for use were those made of cadmium-tin and cadmium-lead alloys containing 15--20 per cent. of cadmium; the lines were sufficiently numerous and distinct, but not too strong,

and there was, moreover, the continuous spectrum between them forming, as it were, a background.

The investigation of tautomeric compounds was in progress, and the results would form the subject of a separate communication to the Society.

***28. "The estimation of nitrites and nitrates by means of ferrous chloride." By A. Wynter Blyth.**

The author has devised an apparatus in which nitrites and nitrates, either singly or together, can be estimated as nitric oxide by means of ferrous chloride. The essential feature of the apparatus is a mercury valve, which is made by connecting one end of a long delivery tube with the side tube of a flask, and causing the other to dip below the surface of mercury in the mercurial trough, the bend of the delivery tube being 770 mm. above this level. The air from the flask is expelled by boiling, and a special feature is made of the ease with which successive vacua can be obtained in such a flask. The author has found that nitric oxide is evolved from nitrites at once, whereas there is an appreciable interval of from one to two minutes before any nitric oxide is formed from nitrates. Nitrates yield the whole of the nitric oxide only when the flask is evacuated several times. The results obtained with the apparatus are accurate.

Discussion.

Mr. J. H. Coste said that eight years ago he had used in the laboratory of the Royal Agricultural Society of England an apparatus similar in principle to that described by the author, but of simpler construction. It was, he believed, devised by Dr. Walter Leather, and was described in Addyman's *Agricultural Analysis*. The india-rubber stopper of the evolution flask was provided with a water jacket, and fitted with a delivery tube considerably over 760 mm. in length, dipping under the surface of mercury in a tray placed at a lower level. The use of the rising tube described by the author was thus obviated. The results obtained and the ease in manipulation left little to be desired.

Mr. Wynter Blyth, in reply, stated that he did not claim anything new in the principle of the apparatus; it had, indeed, been applied for some time in the construction of mercury pumps. He was glad to hear that the same kind of valve was in use successfully elsewhere.

***29. "Estimation of boric acid mainly by physical processes." By A. Wynter Blyth.**

When a methylic alcohol solution of boric acid is distilled, 78 per cent. of the acid collects in the first fifth of the distillate; a dilute aqueous solution, on the contrary, loses very little of the acid until concentration has taken place. These facts are applied to the detection of minute traces of boric acid in various substances.

It is shown that even small quantities of boric acid can be estimated by polarimetric methods. For this purpose, 3 grams of dextrotartaric acid are dissolved in methylic alcohol, and the solution of boric acid in methylic alcohol added so as to make exactly 20 c.c. at 18°. The increase of rotation is then observed. For quantities amounting to 0·05—1·03 per cent., a 5 dm. tube is required. The specific rotation, calculated on the constant amount of the tartaric acid present, is given for quantities ranging from 0·05—3 per cent.

When boric acid is boiled with a solution of sodium carbonate, carbon dioxide is evolved, in accordance with the equation $Na_2CO_3 + 4H_3BO_3 = Na_2B_4O_7 + CO_2 + 6H_2O$, the proportion being 0·177 part by weight for every part of boric acid present. After boiling and concentrating, the solution is made up to a definite volume, and the conductivity at 18° measured by Kohlrausch's method. From the reduction of the resistance, the amount of boric acid, as sodium borate, can be estimated provided the sodium carbonate solution employed is always of the same strength. A table is given of the values of K (resistance of cell divided by resistance, in ohms, of solution), and the results are plotted out as a curve. After the resistance has been determined, an aliquot part or the whole of the solution is transferred to a flask connected with the apparatus described in the preceding abstract, and the carbon dioxide estimated by treatment with an acid.

Discussion.

Mr. A. C. Chapman pointed out that small quantities of impurities in the boric acid would be likely to sensibly affect the accuracy of physical methods such as those suggested by the author, and asked how the whole of the boric acid could be obtained from such substances as food-products in a state of sufficient purity for the application of these methods.

Mr. Wynter Blyth, in reply, said that distillation with methylic alcohol gave the methyl compound in a state of sufficient purity for the purpose of estimation by the polarimetric method.

30. "The interaction of ethylic sodiomalonate and mesityl oxide. A correction." By Arthur W. Crossley.

Since the publication of a preliminary notice on the action of ethylic sodiomalonate on mesityl oxide (*Proc.*, 1898, **14**, 247) Dr. Vorländer of Halle has pointed out to the author that the reaction has already been studied. The substance obtained by hydrolysis of the condensation product is dimethylhydroresorcine, $C_8H_{12}O_2$, and possesses half the molecular weight assigned to it by the author, and although having marked acid properties is not a carboxylic acid.

The author expresses his regret at not having known of Dr. Vorländer's work.

31. "On Lössner's benzoylethyloxysulphocarbamic acid, and the formation of pseudoureas." By Augustus Edward Dixon, M.D.

Benzoyl chloride interacts with a hot saturated solution of potassium thiocyanate, yielding potassium chloride and a compound, $C_{10}H_{11}NSO_2$, regarded by Lössner (*J. prakt. Chem.*, 1874, [ii], 10, 237) as benzoylethyloxysulphocarbamic acid, COPh·NEt·CO·SH. Miquel (*Ann. Chim. Phys.*, 1877, [v], 11, 334), showed later that the same compound is produced from benzoylthiocarbimide and ethylic alcohol, and that consequently it is not an acid, but an 'ether,' COPh·NH·CS·OEt. With caustic potash, it affords a potassium derivative, from which by interaction with ethylic iodide, the corresponding ethylic compound is obtained; the latter is decomposed by ammonia into mercaptan, together with a supposed unsymmetrical benzoylethylurea, COPh·NEt·CO·NH_2.

In the present paper, it is shown that the constitution assigned to this 'urea' is not in accordance with its properties. On hydrolysis, it yields carbonic and benzoic acids, alcohol, and ammonia, but no ethylamine, from which it follows that the ethylic group is not attached to nitrogen, and the conclusion is drawn that the supposed urea of Lössner is really the ethylic salt of a benzoylated imidocarbamic acid, COPh·N:C(OEt)·NH_2. Corresponding compounds have now been obtained, which bear towards the ureas a relation similar to that subsisting between the pseudothioureas and the thiocarbamides: to maintain uniformity of nomenclature, it is proposed that such imido-derivatives of organic salts of carbamic acid should be termed pseudoureas generically.

The constitution attributed by Lössner to the ethylic derivative from which the above ethyl-ψ-*n*-benzoylurea is obtained is COPh·NEt·CO·SEt; its properties, however, are inconsistent with this structure,

and the author assigns reasons for representing it by the formula COPh·N:C(OEt)·SEt. If the potassium compound from which the latter is produced be similarly constituted, Miquel's formula for Lössner's benzoylethyloxysulphocarbamic acid requires further modification into that of the tautomeric ethylic imidobenzoylthiocarbonate, COPh·N:C(OEt)·SH.

Methyl-ψ-n-*benzoylurea*, COPh·N:C(OMe)·NH_2, is deposited from light petroleum in fern-like masses of white, flattened crystals, melting, without decomposition, at 77—78°. When boiled with alkali, or heated with water at 150—160° under pressure, it is hydrolysed into carbonic and benzoic acids, ammonia, and methylic alcohol; no ethylamine could be detected. Its isomeride, ab-*benzoylmethylurea*, COPh·NH·CO·NHMe, is prepared by desulphurising the corresponding thiocarbamide with silver nitrate; the thiocarbamide separates from alcohol in tufts of shining needles, the urea in colourless, thick prisms; they melt at 152° and 171° respectively.

Ethyl-ψ-n-*benzoylurea*, COPh·N:C(OEt)·NH_2, forms rhombohedral crystals melting at 74—75° without decomposition. Its isomeride, *ab*-benzoylethylurea, is stated by Miquel to melt at 192°, or, according to Leuckart (*J. prakt. Chem.*, 1880, [ii], 21, 33), at 168°. When prepared from the thiocarbimide (m. p. 130—131°) by means either of silver nitrate or, as described by Miquel, of yellow oxide of mercury, it was found to melt at 114—115°.

Anisoilthiocarbimide, OMe·C_6H_4·CO·NCS, is obtained, in solution, by heating the corresponding chloride, OMe·C_6H_4·COCl, dissolved in benzene, with lead thiocyanate. It unites with alcohol, forming *anisoilthiourethane* or *ethylic imidoanisoilthiocarbonate*, OMe·C_6H_4·CO·N:C(SH)·OEt, which crystallises in small, white needles melting at 70—71°. The *potassium derivative* of the latter melts at about 222° (uncorr.); when boiled in alcoholic solution with ethylic iodide, and then saturated with ammonia, it yields *ethyl-ψ*-n-*anisoilurea*, OMe·C_6H_4·CO·N:C(OEt)·NH_2, in white, transparent prisms melting at 69—70°.

Anisoilthiocarbimide unites spontaneously with nitrogenous bases forming thioureas and thiocarbamides; the following are described. *Anisoilthiourea*, $CSN_2H_3·C_8H_7O_2$, forms rhombs and octahedra melting at 216—217°. By fusion with chloracetic acid, it yields *anisoilthiohydantoin* [*n*-anisoilthiourantoin (*Trans.*, 1897, 71, 638)], a pale-yellow solid, nearly insoluble in the ordinary solvents, and decomposing between 222° and 230°. ab-*Anisoilphenylthiocarbamide* crystallises from alcohol in brilliant prisms melting at 126°; the corresponding *ortho*- and *para-tolyl* compounds melt at 126·5° and 127—128° respectively. ab-*Anisoilmethylthiocarbamide* melts at 143—144°; the *ethylic* homologue melts at 126·5—127·5°, and yields, on desulphurisa-

tion, the symmetrical urea, $C_6H_7O_2 \cdot NH \cdot CO \cdot NHEt$, isomeric with the above ψ-compound; it melts at 146—147°. *ab-Anisoilbenzylthiocarbamide* forms colourless prisms melting at 127—128°. *n-Anisoil-v-phenylbenzylthiourea*, $C_8H_7O_2 \cdot N{:}C(SH) \cdot NPhBz$, from the thiocarbimide and benzylaniline, occurs in brilliant rhombic plates melting at 142—143°. It is not desulphurised by boiling with alkaline solution of lead, in which respect it differs from the other anisoil thio-compounds described.

32. "On certain isomeric tertiary benzylthioureas." By Augustus Edward Dixon, M.D.

n-Phenyl-v-methylbenzylthiourea, $NPh{:}C(SH) \cdot NMe \cdot CH_2Ph$, was obtained, in quantitative amount, from phenylthiocarbimide and methylbenzylamine; it formed long, brilliant, silvery prisms melting at 129—130°. Its isomerides, $NMe{:}C(SH) \cdot NPhBz$, and $NBz{:}C(SH) \cdot NMePh$, melt at 121° and 85° respectively. By desulphurisation with silver nitrate, it afforded the *urea*, $NHPh \cdot CO \cdot NMeBz$, which crystallised in thin, pearly needles melting at 134—135°.

n-Benzyl-v-methylbenzylthiourea, $NBz{:}C(SH) \cdot NMeBz$, prepared from benzylthiocarbimide and methylbenzylamine, occurred in vitreous needles melting at 73°. Its isomeride, *n-methyl-v-dibenzylthiourea*, $NMe{:}C(SH) \cdot NBz_2$, formed white, rhombic crystals melting at 110—111°.

n-Methyl-v-methylbenzylthiourea, $NMe{:}C(SH) \cdot NMeBz$, formed vitreous, flattened crystals melting at 87·5—88·5°. Its isomeride, *n-benzyl-v-dimethylthiourea*, $NBz{:}C(SH) \cdot NMe_2$, crystallised in vitreous prisms melting at 98·5—99·5°.

These thioureas are practically insoluble in water; they are unaffected by boiling with alkaline lead tartrate, but are readily desulphurised by warming with nitrate of silver. It was remarked in 1893 (*Trans.*, 63, 540) that amongst the then known phenylated isomeric tertiary thioureas, the member containing the NPh-group had the highest melting point; it is now shown that, in the methylphenylbenzyl series, this is also the case.

33. "Is camphene unsaturated?" By J. E. Marsh.

The more recent formulæ for camphor, such as that of Bredt, represent camphene, the typical hydrocarbon of the group, as an unsaturated compound with one double linking. The reactions which appear to support this view are, firstly, the conversion of camphene into camphene glycol, $C_{10}H_{16}(OH)_2$, by the action of potassium permanganate (Wagner, *Ber.*, 1890, 23, 2307), and, secondly, the production of camphene di-

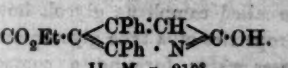
bromide, $C_{10}H_{16}Br_2$, by the action of bromine on camphene (Reychler, *Ber.*, 1896, **29**, 900). These reactions would be sufficient to establish the unsaturated character of camphene if it were a matter quite free from doubt that camphene glycol and camphene dibromide are the simple additive compounds they appear at first sight to be. The so-called camphene glycol, however, appears to possess none of the properties of a true glycol; and, in particular, the fact that it readily loses water, forming a compound having all the properties of an aldehyde, seems to be inconsistent with the view that it is a glycol at all. Moreover, the action of permanganate on camphene is much slower than is usually the case with an unsaturated compound. With regard to camphene dibromide, experiments have been made by the author which lead him to believe that this compound is not formed by the direct union of bromine and camphene, but is really the product of the interaction of bromine and camphene hydrobromide. By saturating camphene dissolved in glacial acetic acid with hydrogen bromide, and then adding bromine to the product, the so-called camphene dibromide is obtained in amount equal to about 70 per cent. of the theoretical yield, whereas Reychler, by the direct action of bromine on camphene, obtained only 8 grams from 27·7 grams of camphene, which represents a yield of about 13 per cent. The chief product of the action of bromine on camphor is the substituted derivative bromocamphene, $C_{10}H_{15}Br$. In this reaction, then, it appears that bromine first replaces hydrogen in camphene, forming bromocamphene and hydrogen bromide; the hydrogen bromide is partly given off in the gaseous form, but in part also combines with the excess of camphene, forming camphene hydrobromide, which is then further acted on by bromine, giving the so-called camphene dibromide by the substitution of bromine for hydrogen. This reaction, therefore, cannot be brought forward as evidence in favour of the unsaturated character of camphene. It may be argued, perhaps, that the direct union of camphene with hydrogen bromide is in itself sufficient evidence of its unsaturated character. It does not, however, appear to be consistent with the nature of the double linking that it should resist the action of bromine and succumb to that of hydrogen bromide. Such a property is far more characteristic of the trimethylene ring, as Professor Perkin has shown, and may be characteristic also of other ring formations.

34. "Formation of α-pyrone compounds and their transformation into pyridine derivatives." By Siegfried Ruhemann.

The substances formed from α-pyrone derivatives by the addition of two molecular proportions of ammonia (*Proc.*, 1899, 15, 6), have been transformed into pyridine compounds. The view already

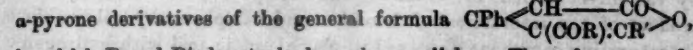
expressed, that these additive products may be regarded as ammonium salts of unsaturated amino-acids, readily explains such a change. The transformation is effected by preparing from the ammonium salts the corresponding ethylic salts, which, on distillation, lose alcohol and condense to the pyridine compounds represented by the formulæ:

I. M. p. 184°.



II. M. p. 210°.

From the ethylic salt represented by formula I., the corresponding acid was prepared; this loses carbon dioxide at 240°, forming phenylmethylpyridone (m. p. 207—208°).

β-Diketones, like ethylic salts of β-ketonic acids, condense with ethylic phenylpropiolate under the influence of sodium ethoxide, forming α-pyrone derivatives of the general formula  , in which R and R′ denote hydrocarbon radicles. Thus, from acetylacetone and from benzoylacetone, compounds have been obtained which melt respectively at 128° and 143—144°, and behave like α-pyrone derivatives with alcoholic ammonia.

ANNIVERSARY MEETING.

The Anniversary Meeting will be held on Wednesday, March 29th, at 3 o'clock in the afternoon.

NOTICE TO AUTHORS.

As the *Proceedings* go to press on the Monday after each ordinary Meeting of the Society, the announcement of papers for the next Meeting cannot be made in this publication unless the papers are in the hands of the Secretaries by noon on that day.

At the next meeting, on Thursday, March 2nd, 1899, the following papers will be communicated:—

"Bromomethylfurfuraldehyde." By H. J. H. Fenton, M.A., and Mildred Gostling, B.Sc.

"The action of metallic thiocyanates on certain substituted carbamic and oxamic chlorides, and a new method for the production of thiobiurets." By Augustus Edward Dixon, M.D.

"Ethylic ββ-dimethylpropanetetracarboxylate." By W. Trevor Lawrence.

"The action of alkyl iodides on hydroxylamine." By Wyndham R. Dunstan, F.R.S., and Ernest Goulding, B.Sc.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 15. **No. 205.**

March 2nd, 1899. Professor Dewar, F.R.S., President, in the Chair.

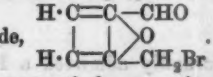
Mr. John S. MacArthur was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Clement Harrison Baker, Athelney, Featherstone Road, King's Heath, Birmingham; Frederick James Beale, Wilderspool Brewery, Warrington; Alfred Ernest Bond, Prince's Chambers, Corporation Street, Birmingham; Charles Robert Darling, 220, Eglinton Road, Plumstead; Percy Haigh, 312, Romford Road, Forest Gate, E.; Thomas Judge, 142, Waller Road, New Cross, S.E.; William McConnell, 178, Springfield Road, Glasgow; Wilfred Walter Morris, Newtown St. Boswells, Roxburghshire, N.B.; Maurice Emile Schweich, 85, Belgrave Road, S.W.; Edward Thomas Shelbourn, 1, Chalcot Crescent, Regent's Park Road, N.W.; Richard Threlfall, 45, Frederick Road, Edgbaston, Birmingham; Ernest Albert Tyler, Warsop, Mansfield, Notts.

Of the following papers, those marked * were read.

***35. "Bromomethylfurfuraldehyde." By H. J. H. Fenton, M.A., and Mildred Gostling, B.Sc.**

It has been shown by the authors in a previous communication (*Trans.*, 1898, 73, 556) that certain carbohydrates, when acted on by hydrogen bromide in ethereal solution, give rise to a beautiful, purple coloration. From observations made with a considerable number of typical carbohydrates, it would appear that the rapid production of

this intense colour is characteristic of ketohexoses, or substances capable of yielding them by hydrolysis. The colour-producing substance has now been isolated in a pure state, and is obtained in the form of short, golden-yellow, prismatic crystals belonging to the oblique system. It melts at 60°, decomposes somewhat explosively at a higher temperature, and is practically insoluble in cold water, but dissolves easily in most organic solvents, giving solutions which powerfully stain the skin. Its solutions give a bright orange colour with aniline acetate after some time; they powerfully reduce silver and copper solutions, react with phenylhydrazine, and when treated with an ethereal solution of hydrogen bromide, produce an intense purple coloration, which is exactly similar to, but appears even more quickly than, that obtained with ketohexoses. Analysis and molecular weight determinations show that it has the formula $C_6H_5BrO_2$, and its reactions and properties indicate that it is a bromomethylfurfuraldehyde,  . On oxidation with silver oxide, it yields ω-hydroxymethylpyromucic acid identical with that obtained by Hill and Jennings from the corresponding bromo-acid (*Amer. Chem. J.*, 1893, 15, 162). The whole of the bromine is precipitated by an alcoholic solution of silver nitrate, and from the solution a substance is obtained which closely resembles, but seems to be isomeric with, the hydroxymethylfurfuraldehyde of Düll and Kiermayer (*Chem. Zeit.*, 1895, 19, 206, 1003); a similar result is obtained by heating the substance with water in presence of barium carbonate. If the substance be covered with water and saturated with sulphur dioxide, it slowly dissolves, and the solution, after remaining for some hours, gives, on extraction by ether, a product which crystallises from hot water in yellow needles; these melt at 117°, and in solution give a magnificent blue colour with caustic alkalis. Analysis and molecular weight determinations indicate that this is a condensation product, and is free from bromine; its constitution is now being investigated.

***36. "The reaction of alkyl iodides with hydroxylamine. Formation of alkylated hydroxylamines and oxamines." By Wyndham R. Dunstan, F.R.S., and Ernest Goulding, B.Sc.**

As the authors have shown previously (*Proc.*, 1894, 10, 138; *Trans.*, 1896, 69, 839), methyl iodide readily reacts with hydroxylamine, forming hydriodides of hydroxylamine and the hydriodide of a trimethyl derivative. The hydrated base crystallises well and melts sharply at 96°. It is not volatile. The anhydrous base has not yet been isolated. The aqueous solution is strongly alkaline, and

does not reduce Fehling's solution. Solution of silver nitrate is only reduced on warming, or after prolonged standing. Dimethylamine and formaldehyde are produced by the action of hydriodic acid, but no methyl iodide. The same decomposition ensues when the base (or its salts) is heated either alone or with dilute sulphuric acid, $(CH_3)_3NO = CH_2O + NH(CH_3)_2$. When allowed to stand in aqueous solution in contact with zinc dust, it is reduced to trimethylamine, $(CH_3)_3NO + H_2 = (CH_3)_3N + H_2O$.

The principal salts of the base are described.

The authors conclude that this substance is not a true trimethylhydroxylamine, but a *trimethyloxyammonia* or *trimethyloxamine*, $(CH_3)_3N{:}O$.

By the reaction of methyl iodide with trimethyloxamine, the iodide of a tetramethyl derivative is produced. The free base, which is strongly alkaline, has, so far, been obtained only in aqueous solution. The salts crystallise well.

When the solution of a salt is warmed with an alkali, methyl alcohol is split off and trimethyloxamine is formed, $N(CH_3)_3OCH_2OH = N(CH_3)_3O + CH_3OH$.

When the aqueous solution of a salt is heated at 150° in a closed tube, trimethylamine and formaldehyde are produced, $N(CH_3)_3OCH_2OH = N(CH_3)_3 + CH_2O + H_2O$.

When the iodide is heated with concentrated hydriodic acid, the products are methyl iodide, dimethylamine, and formaldehyde, $N(CH_3)_3OCH_2OH + HI = NH(CH_3)_2 + CH_3I + CH_2O + H_2O$.

When reduced in aqueous solution with zinc dust, trimethylamine and methyl alcohol are formed, $N(CH_3)_3OCH_2OH + H_2 = N(CH_3)_3 + CH_3OH + H_2O$.

The base is, therefore, *trimethylmethoxyammonium hydroxide*, $(CH_3)_3N{\cdot}OCH_2{\cdot}OH$.

When ethyl iodide reacts with hydroxylamine, hydriodides of hydroxylamine are formed, together with a *diethylhydroxylamine hydriodide*. The base is an oily liquid with a curious aromatic odour, boiling, with some decomposition, between 130—134°. Its aqueous solution is strongly alkaline, and acts as a powerful reducing agent. The salts are fully described; the oxalate, $[(C_2H_5)_2NOH]_2H_2C_2O_4$, crystallises very readily and melts at 136—137°. When heated, it decomposes into ethylamine and acetaldehyde, $(C_2H_5)_2NOH = C_2H_5NH_2 + C_2H_4O$. When heated with hydriodic acid, diethylamine is formed, but no ethyl iodide. It forms an acetyl derivative. The substance is, therefore, a true *β-diethylhydroxylamine*, $N(C_2H_5)_2OH$. It is isomeric with the two diethylhydroxylamines described by Lossen (NHEtOEt), but is probably identical with the substance obtained by Kissel by the action of zinc ethyl on nitroethane. The substance

now described closely resembles in its decompositions the β-dibenzylhydroxylamine studied by Behrend and Leuchs.

By the reaction of diethylhydroxylamine with ethyl iodide, the hydriodide of a triethyl derivative is obtained. The base is crystalline and non-volatile. The aqueous solution is strongly alkaline. It does not reduce Fehling's solution, but reduces silver nitrate on warming. The principal salts are fully described. In all its reactions, this base closely corresponds with trimethyloxamine. When heated, it breaks up into diethylamine and acetaldehyde; when reduced with zinc dust in aqueous solution, it furnishes triethylamine, whilst by the action of hydriodic acid it is converted into triethylamine without the formation of ethyl iodide. This substance is, therefore, *triethyloxyammonia* or *triethyloxamine*, $(C_2H_5)_3N{:}O$. It is not identical with the isomeride of triethylhydroxylamine which Bewad describes as resulting from the action of zinc ethyl on nitroethane.

Similarly, normal propyl iodide and secondary propyl iodide react with hydroxylamine, forming *dipropyl-* and *di-isopropylhydroxylamines*, $(C_3H_7)_2NOH$.

Hantzsch and Hilland (*Ber.*, 1898, 31, 2058) have recently described their work on this subject. They generally confirm the account given by the authors five years ago of the reaction of methyl iodide with hydroxylamine. They assert that the hydrated base (see above) is really a carbonate. The authors have repeated their experiments, and find that there is no foundation for this statement. It is evident, from the different account given by Hantzsch and Hilland of the properties of trimethyloxamine, that the material they examined contained impurity, probably hydroxylamine.

By the reaction of ethyl iodide with hydroxylamine, Hantzsch and Hilland obtained only monethylhydroxylamine hydriodide. The authors have repeated their experiments, and have been unable to isolate any such substance. They find, as stated above, that diethylhydroxylamine is the chief product of the reaction.

Discussion.

Dr. Hewitt drew attention to Bamberger's recent discovery of the analogous dimethylaniline oxide by the direct oxidation of dimethylaniline by hydrogen peroxide (*Ber.*, 1899, 32, 342). The substance is destitute of reducing properties, and exhibits a peculiar transformation into a mixture of ortho- and para-nitrodimethylanilines by the action of nitrous acid. This transference of an oxygen atom from the dimethylamino- to the nitroso-group, thereby converting it into a nitro-group, may possibly be the analogue of the conversion of trimethyloxamine into a mixture of dimethylamine and formaldehyde.

Dr. FORSTER remarked that distillation under atmospheric pressure resolves the benzyl ether of camphoroxime into benzaldehyde and camphorimine, a change suggesting analogy with the conversion of trimethyloxamine into formaldehyde and dimethylamine.

***37. "Derivatives of αα′-dibromocamphorsulphonic acid." By Arthur Lapworth.**

When ammonium α-bromocamphorsulphonate is heated with bromine and water at 110—120°, a dibromocamphorsulphonic acid is produced, identical with that obtained in small quantities by heating the salt with dilute nitric acid (*Trans.*, 1897, 71, 19; compare *Proc.*, 1898, 14, 159), and its investigation has been continued with the following results.

The *ammonium*, *potassium*, *sodium*, *calcium*, *barium*, *zinc*, *cadmium*, and *lead* salts are readily soluble in water and crystallise well; the *basic lead* salt is amorphous, and is practically insoluble in water. *αα′-Dibromocamphorsulphonic chloride*, $C_{10}H_{13}Br_2O{\cdot}SO_2Cl$, is very sparingly soluble in the usual media; it crystallises in beautiful, hemihedral forms belonging to the orthorhombic system, is isomorphous with the sulphonic bromide already described (*loc. cit.*), and melts at 203—204° with decomposition. The *amide*, $C_{10}H_{13}Br_2O{\cdot}SO_2NH_2$, forms hemihedral crystals, is very sparingly soluble in the ordinary media, and melts at about 238° with decomposition.

When αα′-dibromocamphorsulphonic chloride is treated with piperidine in ethereal solution, a mixture of *dibromocamphorsulphopiperidide*, $C_{10}H_{13}Br_2O{\cdot}SO_2NC_5H_{10}$, and *monobromocamphorsulphopiperidide*, $C_{10}H_{14}BrO{\cdot}SO_2NC_5H_{10}$, is obtained. The former crystallises in orthorhombic plates or prisms melting at 157—158°; the latter, which may also be obtained by the action of piperidine on α-monobromocamphorsulphonic chloride, crystallises in plates melting at 152°.

When dibromocamphorsulphonic acid is heated with strong alkalis, bromine is eliminated, and the product, on treatment with phosphorus pentachloride, yields α-monobromocamphorsulphonic chloride melting at 135°, the action being exactly analogous to that of alcoholic potash or soda on αα′-dibromocamphor.

When heated at its melting point, αα′-dibromocamphorsulphonic bromide loses sulphur dioxide, yielding *αα′π-tribromocamphor*, $C_{10}H_{13}Br_3O$. This crystallises from dilute alcohol in fine needles and melts at 69—70°; it is rapidly decomposed when warmed with solutions of silver salts or with alkalis, the product with the latter being απ-dibromocamphor melting at 152°. The new tribromocamphor is also obtained by heating απ-dibromocamphor with bromine at 120°

in sealed tubes; this fact and others which have been mentioned indicate that the dibromocamphorsulphonic acid has the constitution assigned to it by the author.

38. "Ethylic ββ-dimethylpropanetetracarboxylate." By W. Trevor Lawrence.

Meyenburg (private communication, compare *Ber.*, 1895, **28**, 785) attempted to prepare ethylic ββ-dimethylpropanetetracarboxylate by the condensation of ethylic isopropylenemalonate with ethylic sodiomalonate, but was unsuccessful, and, with his permission, the author has continued the work.

Ethylic ββ-dimethylpropanetetracarboxylate, $CMe_2[CH(CO_2Et)_2]_2$, is formed in small amount in preparing ethylic isopropylenemalonate from acetone and ethylic malonate in the presence of acetic anhydride and zinc chloride. It is obtained readily by the interaction of molecular quantities of ethylic isopropylenemalonate with ethylic sodiomalonate in dry ethereal or benzene solution. The mixture is allowed to boil during 24 hours, a half molecular proportion of ethylic sodiomalonate added, and the boiling continued during a further 24 hours. On fractional distillation in a vacuum, the compound is obtained as a thick oil boiling at 218° under 14 mm. pressure. On hydrolysis with alcoholic potash, it is converted into ββ-dimethylpropanetricarboxylic acid, $CO_2H\cdot CH_2\cdot CMe_2\cdot CH(CO_2H)_2$, melting at 172°, and with sulphuric acid into ββ-dimethylglutaric acid, $CO_2H\cdot CH_2\cdot CMe_2\cdot CH_2\cdot CO_2H$, melting at 101°, from which the anhydride melting at 123° was obtained.

The author is engaged with Dr. Herz in the further investigation f the properties of the substance

39. "The action of metallic thiocyanates on certain substituted carbamic and oxamic chlorides; and a new method for the production of thiobiurets." By Augustus Edward Dixon, M.D.

Acid chlorides containing the group COCl interact with metallic thiocyanates, in presence of suitable solvents, yielding the corresponding organic isothiocyanates; chlorine united with certain groups, other than carbonyl, is similarly exchangeable, but complete dechlorination is generally hard to effect. Experiments made with a view of ascertaining whether the halogen in substances generally acidic in character, or only that in direct union with a negative group could thus be substituted, pointed to the latter as the determinant condition.

By heating with mercuric thiocyanate in presence of cumene, the chlorides of disubstituted carbamic acids are converted into isothio-

cyanates of the form $NR_2 \cdot CO \cdot NCS$; these substances are related to the thiobiurets and to thioallophanic acid in the same way as ordinary thiocarbimides to thiocarbamides and thiocarbamic acid respectively. They unite spontaneously with nitrogenous bases, affording substituted thiobiurets, and with benzylic alcohol, forming the corresponding substituted thioallophanates, $NR_2 \cdot CO \cdot NH \cdot CS \cdot OBz$.

These thiobiurets may be regarded as thiocarbamides containing the carbamyl or $NR_2 \cdot CO$-group; if so, the rule formulated by the author with respect to desulphurisation of the thiocarbamides by alkaline lead tartrate (*Trans.*, 1893, 63, 318) holds good, the carbamyl group here playing the same part as an alkylic or allylic radicle. Thus, the thiobiurets, $NR_2 \cdot CO \cdot NH \cdot CS \cdot NHX$, can be desulphurised when X is an aromatic radicle, but not when it is aliphatic. Their behaviour as carbamylthiocarbamides (or thioureas) is further instanced by the production of thiohydantoin-like [derivatives on treatment with chloracetic acid; the latter compounds are related to the biurets in the same way as the thiohydantoins to the thiocarbamides, and, in like manner, yield thioglycollic acid on hydrolysis.

The isothiocyanates could not be freed from the accompanying cumene by distillation either with steam or under diminished pressure; their solutions were used in preparing the following derivatives.

(1) *Diphenylcarbamylisothiocyanate*, $NPh_2 \cdot CO \cdot NCS$, with aniline gives *acc-triphenylthiobiuret*, $NPh_2 \cdot CO \cdot NH \cdot CS \cdot NHPh$, crystallising in white needles which melt at 163—163·5° and yield phenylthiocarbimide when heated with acetic anhydride. *a-Orthotolyl-c-diphenylthiobiuret*, $NPh_2 \cdot CO \cdot NH \cdot CS \cdot NHTo$, from orthotoluidine, occurs in fine, white needles melting at 163·5—164°. When desulphurised by silver nitrate, it affords the corresponding *biuret*, $NPh_2 \cdot CO \cdot NH \cdot CO \cdot NHTo$, melting at 132—133°. *a-Paratolyl-c-diphenylthiobiuret* melts at 172—172·5°, and resembles generally the ortho-derivative. *a-Methyl-c-diphenylthiobiuret* melts at 170—171°; the *ethylic* homologue at 137—138°, and the corresponding *benzylic* derivative at 167—168°. *c-Diphenylthiobiuret*, $NPh_2 \cdot CO \cdot NH \cdot CS \cdot NH_2$, is precipitated on mixing the calculated quantity of alcoholic ammonia with the isothiocyanate solution; it forms long, yellow prisms melting at 183°, and when fused with chloracetic acid, yields *n-diphenylcarbamylthiourantoin*, $NPh_2 \cdot CO \cdot N{:}C\langle \begin{matrix} S—CH_2 \\ NH \cdot CO \end{matrix} \rangle$ (*Trans.*, 1897, 71, 638), which is deposited from alcohol in tufts of flexible needles, melts at 184—185°, and is hydrolysed by potash, forming thioglycollic acid. *a-Benzylphenyl-c-diphenylthiobiuret*, $NPh_2 \cdot CO \cdot NH \cdot CS \cdot NPhBz$, from benzylaniline, occurs in white needles, becoming electrical on friction and melting at 137—138°. *a-Diphenylcarbamyl-β-phenylthiosemicarbazide*, $NPh_2 \cdot CO \cdot NH \cdot CS \cdot NH \cdot NHPh$, melts at 152·5—153°. *Benzylic*

a-*diphenyl-β-thioallophanate*, from the isothiocyanate and benzylic alcohol, occurs in vitreous, apparently rhombic, prisms melting at 141—142°; attempts to form similar compounds with methylic, ethylic, and cinnamic alcohols failed.

(2) *Methylphenylcarbamylisothiocyanate*, NMePh·CO·NCS, with aniline, yields a-*phenyl*-c-*methylphenylthiobiuret*, NMePh·CO·NH·CS·NHPh, in woolly masses of needles melting at 158—159°. a-*Orthotolyl*-c-*methylphenylthiobiuret* forms thick, vitreous prisms melting at 108°; the *paratolyl* derivative occurs in white, glistening plates melting at 156—157°. ac-*Dimethylphenylthiobiuret* forms leafy crystals melting at 90—91°. c-*Methylphenylthiobiuret*, NMePh·CO·NH·CS·NH_2, crystallises in brilliant, apparently clinorhombic, prisms melting at 166—167°; with chloracetic acid, it yields n-*methylphenylcarbamylthiourantoin*, NMePh·CO·N:C$<^{S—CH_2}_{NH·CO}>$ a yellowish, crystalline powder melting at 199—200°, and giving thioglycollic acid on hydrolysis. a-*Methylphenylcarbamyl-β-phenylthiosemicarbazide* crystallises from alcohol in brilliant prisms, melting at 119—120°; no evidence was obtained of the production of a stereo-, or other, isomeride. *Benzylic* a-*methylphenyl-β-thioallophanate*, NMePh·CO·NH·CS·OBz, forms vitreous rhombohedra melting at 90—91°.

(3) *Ethylphenylcarbamylisothiocyanate*, NEtPh·CO·NCS, forms the following derivatives:—a-*Phenyl-γ-ethylphenylthiobiuret*, melting at 106—107°; the *orthotolyl* and *paratolyl* compounds, melting at 124—125° and 174° respectively. c-*Ethylphenylthiobiuret* occurs in large, greasy-looking, flattened prisms melting at 147—148°, and yielding, with chloracetic acid, n-*ethylphenylcarbamylthiourantoin*, melting at 184—185°. *Benzylic*-a-*ethylphenyl-β-thioallophanate* crystallises in colourless prisms melting at about 120°.

(4) *Benzylphenylcarbamylisothiocyanate*, NPhBz·CO·NCS, resembles its congeners in forming a yellowish solution which has no distinctive odour, and can be desulphurised in the cold by ammoniacal nitrate of silver, or by boiling with alkaline lead tartrate. a-*Phenyl*-c-*benzylphenylthiobiuret*, NPhBz·CO·NH·CS·NHPh, occurs in colourless prisms melting at about 103°; the corresponding a-*orthotolyl* compound melts at 131—132°, and when desulphurised, in presence of ammonia, by silver nitrate, yields a *guanidine*, NPhBz·CO·NH·C(NH)·NHTo, melting at 136—136·5°. a-*Methyl*-c-*benzylphenylthiobiuret* forms white prisms melting at 99—100°; the a-*ethyl* derivative melts at 67—68°. c-*Benzylphenylthiobiuret* crystallises from a mixture of chloroform and alcohol in lustrous, rectangular prisms; it melts at 179—180°, and with chloracetic acid, yields the compound, NPhBz·CO·N:C$<^{S—CH_2}_{NH·CO}>$, a sandy, crystalline powder melting between 194° and 195°, and

affording thioglycollic acid on hydrolysis by potash. *Benzylic α-benzylphenyl-β-thioallophanate* separates from hot alcohol in brilliant, vitreous prisms melting at 133—134°.

(5) *Oxanilylisothiocyanate*, NHPh·CO·CO·NCS, is obtained from phenyloxamic (oxanilic) chloride and lead thiocyanate in presence of toluene; its solution, when mixed with aniline, yields *α-phenyloxamyl-β-phenylthiocarbamide*, NHPh·CO·CO·NH·CS·NHPh; it melts at 172—173°, and slowly dissolves in hot potash; producing phenylthiourea.

40. "A reaction of some phenolic colouring matters." By A. G. Perkin.

In a preliminary communication (*Proc.*, 1898, **14**, 56) it was shown that some phenolic colouring matters which dye mordanted fabrics decompose the alkaline acetates in presence of alcohol, forming monosubstituted salts. The present investigation indicates the general nature of this reaction in the case of colouring matters having hydroxyl radicles in relatively ortho-positions, although in the flavone groups some exceptions occur. In the following list of the salts prepared, those of calcium and barium have been formed by double decomposition from the alkali compounds. The colour and crystalline form are given only in the case of the potassium salt, and all were obtained crystalline unless otherwise stated.

Anthraquinone Group.—Potassium alizarine, $C_{14}H_7O_4K$, violet needles; sodium alizarine, $C_{14}H_7O_4Na$; barium alizarine, $(C_{14}H_7O_4)_2Ba$; calcium alizarine, $(C_{14}H_7O_4)_2Ca$, and potassium monobromalizarine, $C_{14}H_6BrO_4K$. Potassium anthragallol, $C_{14}H_7O_5K$, violet-black needles; also $C_{14}H_7O_5Na$; $(C_{14}H_7O_5)_2Ba$ (amorphous), and $(C_{14}H_7O_5)_2Ca$ (amorphous). Potassium purpurine, $C_{14}H_7O_5K$, and sodium purpurine, $C_{14}H_7O_5Na$, red needles. Potassium anthrapurpurine, $C_{14}H_7O_5K$, red needles. Other colouring matters of this group behave similarly, but quinizarine and metahydroxyanthraquinone do not give the reaction.

Flavone Group.—Morin yields the orange-yellow compounds, $C_{15}H_9O_7K$; $C_{15}H_9O_7Na$; $(C_{15}H_9O_7)_2Mg$; $(C_{15}H_9O_7)_2Ba$; $C_{15}H_5Br_4O_7K$; $C_{15}H_4Br_4O_7K_2$ (amorphous), and quercetin, $C_{15}H_9O_7K$; $C_{15}H_9O_7Na$; $(C_{15}H_9O_7)_2Ba$(?); $C_{15}H_7Br_2O_7K$, orange coloured. Rhamnetin and rhamnazin are peculiar, and give respectively the salts $C_{16}H_{12}O_7$, $C_{16}H_{11}O_7K$ and $C_{17}H_{14}O_7$, $C_{17}H_{13}O_7K$. Potassium rutin, $C_{27}H_{31}O_{16}K$; potassium violaquercitrin, $C_{27}H_{29}O_{15}K$; potassium myrticolorin, $C_{27}H_{27}O_{16}K$, and potassium xanthorhamnin, $C_{28}H_{36}O_{17}$, $C_{28}H_{35}O_{17}K$(?), are yellow, amorphous powders. Fisetin forms $C_{15}H_9O_6K$, yellow needles, and myricetin, $C_{15}H_{10}O_8$, and luteolin, $C_{15}H_{10}O_6$, behave similarly, the

latter with production of very soluble salts. Apigenin, $C_{15}H_{10}O_5$, and chrysin, $C_{15}H_{10}O_4$, do not give the reaction.

In the *xanthone* group, gentisin and euxanthone do not yield salts in this manner, but galloflavin (Bohn and Graebe, *Ber.*, 1887, 20, 1329), a possible member, forms the salt, $C_{13}H_4O_9K_2$, described previously. Maclurin, $C_{13}H_{10}O_6$ (pentahydroxybenzophenone), gives a readily soluble compound, and alizarine yellow A (trihydroxybenzophenone) the salt $C_{13}H_9O_4K$. Cotoin and phloretin do not give the reaction.

Potassium and sodium hæmatein, $C_{16}H_{11}O_6K$, and $C_{16}H_{11}O_6Na$, are described, but compounds of brazilein, $C_{16}H_{12}O_5$, are too soluble for isolation. Santalin, $C_{15}H_{14}O_5$ (?), forms $C_{30}H_{27}O_{10}K$ (amorphous) and curcumin appears to form an analogous compound. From morin, quercetin, and alizarine, alkali salts are formed by boiling alcoholic potash, by carbonates, nitrites, succinates, lactates, benzoates, and salicylates in the presence of absolute alcohol, and by potassium acetate in the cold. Morin appears to form the compound $(C_{15}H_{10}O_7)_2,C_2O_4K_2$ with potassium oxalate. The salts of the anthraquinone group dissolve unchanged in boiling water; those of the flavone, xanthone, and benzophenone groups are decomposed, forming the colouring matter.

From potassium alizarine, $C_{14}H_7O_4K$, the ethers $C_{14}H_7O_3\cdot OMe$ and $C_{14}H_7O_3\cdot OEt$ are formed from the iodides at 230°. Ethylanthragallol, $C_{14}H_7O_4\cdot OEt$, was also obtained. These contain the alkyl group in the meta-position, have previously been prepared by Schunck and Marchlewski (*Trans.*, 1894, 65, 185), and by Liebermann and Jellineck (*Ber.*, 1888, 21, 1169), and indicate the position of the acidic hydroxyl.

Monomethyl purpurine, $C_{14}H_7O_4\cdot OMe$, evidently [OH : OCH_3 : OH = 1 : 2 : 4], forms red needles melting at 228—230°. Ethers of quercetin were not isolated in this manner, in consequence of accompanying decomposition.

To account for the acidic nature of these colouring matters, a change in the quinonoid form is suggested, capable of existence only in the form of a salt. Such a constitution has previously been proposed (*Trans.*, 1896, 69, 1439) to explain the acid compounds of the flavone group, and a comparison of the *acid* and *basic* properties of these colouring matters reveals important points of resemblance.

Potassium alizarine, $C_{14}H_7O_4K$, is converted by cold acetic anhydride into *monacetylalizarine*, $C_{14}H_7O_4Ac$, crystallising in orange-yellow needles which melt at 198—201°; when allowed to remain some weeks with the reagent, diacetylalizarine is produced. Potassium-morin in the cold forms *tetracetylmorin*, $C_{15}H_6O_7Ac_4$, which crystallises in colourless, prismatic needles, melts at 142—145°, and subsequently passes into a very soluble derivative. Potassium quercetin, $C_{15}H_9O_7K$, similarly gives *triacetylquercetin*, $C_{15}H_7O_7Ac_3$, melting at 167—169°,

and quercetin sulphate, $C_{15}H_{10}O_7.H_2SO_4$, a *tetracetyl* compound which forms colourless needles melting at 193—194°.

The salts of morin and quercetin (Hlasiwetz and Pfaundler, *Jahresb.*, 1864, 560), of quercitrin (Liebermann and Hamburger, *Ber.*, 1879, 12, 1179), of fisetin (Schmid, *Ber.*, 1886, 19, 1739), and curcumin (Jackson and Menke, *J. Amer. Soc.*, 1882, 4, 77) appear to have been mixtures, as their percentage composition, though coinciding with the older formulæ of these colouring matters, does not agree with that required by their correct molecular weight.

41. "Note on the optical activity of gallotannic acid." By Otto Rosenheim, Ph.D., and Philip Schidrowitz, Ph.D.

In a recent communication (*Trans.*, 1898, 73, 878), the authors stated that the optical activity of gallotannic acid was first observed by F. M. Flawitzky, and that Günther independently rediscovered it in 1895, Flawitzky's communication remaining unnoticed. During the course of an investigation on the formation of gallic acid from gallotannic acid by the action of moulds, one of the authors (R.) has found that the merit of having first discovered the optical activity of the substance undoubtedly belongs to Ph. van Tieghem, who in a paper on "Fermentation du Tannin," says: "*Je me suis assuré que le tannin dévie vers la droite le plan de polarisation de la lumière incidente,*" and (*Ann. des Sciences Nat.*, 1867, [v], 8, 210) gives the specific rotation of the acid as $[\alpha]_{D16°} + 38{\cdot}1°$. This communication seems to have been unknown to Schiff, who six years later (*Annalen*, 1873, 170, 75) devised the accepted gallotannic acid formula, and directly alluded to the 'inactivity' of this substance, quoting F. W. Krecke's observations (*Arch. Néerl.*, 1871, 6, 193). It is remarkable that the important optical properties of this substance have been thrice discovered independently, and that until quite recently these have not become generally known and are not mentioned in any of the best known text- or hand-books. The fact that van Tieghem did not mention his discovery in a report on the subject (*Compt. rend.*, 1867, 65, 109), and that his original communication appeared in a botanical journal more or less inaccessible to chemists, may account in part for this omission.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Atwater, W. O., and Langworthy, C. F. A Digest of Metabolism Experiments, in which balance of income and outgo was determined. Pp. 434. 8vo. Washington 1898. U.S. Department of Agriculture, Bulletin No. 45 (revised edition). From the Department.

Dufet, H. Recueil de Données Numériques publié par la Société Française de Physique. Deuxième Fascicule. Propriétés Optiques des Solides. Pp. vi + 418—785. 8vo. Paris 1899.

From the Society.

Riban, J. Traité d'Analyse Chimique quantitative par Electrolyse. Pp. vi + 304, avec 96 figures dans le texte. 8vo. Paris 1899.

From the Publishers.

Roscoe, H. E., und Schorlemmer, C. Ausführliches Lehrbuch der Chemie. Fortgesetzt von J. W. Brühl. Fünfter Band. Die Kohlenwasserstoffe und ihre Derivate, oder organische Chemie. Dritter Theil. Bearbeitet in Gemeinschaft mit Edvard Hjelt und Ossian Aschan. Zweite Abtheilung. Pp. 465—1048 + xi. 8vo. Braunschweig 1896.

—— Sechster Band. do. Vierter Theil. do. Pp. xii + 709. 1898.

From the Publishers.

ANNIVERSARY MEETING.

The Anniversary Meeting will be held on Wednesday, March 29th, at 3 o'clock in the afternoon.

NOTICE TO AUTHORS.

As the *Proceedings* go to press on the Monday after each ordinary Meeting of the Society, the announcement of papers for the next Meeting cannot be made in this publication unless the papers are in the hands of the Secretaries by noon on that day.

At the next meeting, on Thursday, March 16th, 1899, the following papers will be communicated:—

"Influence of substitution on specific rotation in the bornylaminic series." By M. O. Forster, Ph.D.

"Rotatory power of optically active methoxy- and ethoxy-propionic acids prepared from active lactic acid." By Thomas Purdie, F.R.S., and James C. Irvine, B.Sc.

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PROCEEDINGS
OF THE
CHEMICAL SOCIETY.
EDITED BY THE SECRETARIES.

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March 16th, 1899. Professor Dewar, F.R.S., President, in the Chair.

Messrs. E. Szarvasy, E. B. Fairweather and Arnold Stevenson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frank Belton, 103, Lower Seedley Road, Pendleton, Manchester; Robert D. Connell, 38, Chapel Road, Stamford Hill, N.; Harold Francis Carl Goltz, 7, Craster Road, Upper Tulse Hill, S.W.; Robert William Lindsey, 22, Hilldrop Crescent, Camden Road, N.; James MacLeod, Westhill, Cardeross Road, Dumbarton; Allan Frederick Walden, New College, Oxford.

The PRESIDENT announced that he desired to present to the Society a daguerreotype of Dalton, which was one of two taken in 1842. The daguerreotype came into the possession of Mr. Dancer, a philosophical instrument maker of Manchester, who, it might be interesting to state, constructed Joule's thermometers and apparatus, and it was from Mr. Dancer's relatives that he had acquired the portrait. He felt that so interesting a memorial of such a man ought not to remain in the possession of a private individual, and it seemed fitting that its custody should be entrusted to the Chemical Society; he therefore presented it to the Society on the understanding that steps should be taken to ensure its safe preservation.

Through the kindness of Mr. S. W. Woolley, he had received an interesting card which appeared to have been used by Dalton during the meeting of the British Association at Manchester in 1842. This card bears his autograph and an embossed head. Accompanying it was an engraved sheet of symbols representing atomic combinations, which had been prepared to illustrate a paper read by Dalton at this meeting. These he also desired to present to the Society, to be included in the collection of memorials of illustrious chemists which was being gradually formed.

On behalf of the meeting, Professor TILDEN thanked the PRESIDENT for the gift of the daguerreotype, which would be preserved with all the

care and solicitude which such an interesting memorial deserved. He added that he believed the well known portrait of Dalton engraved by Jeans, and appearing as the frontispiece in Roscoe and Schorlemmer's Treatise on Chemistry, was prepared from a drawing made from this daguerreotype.

Of the following papers, those marked * were read.

*42. "The boiling point of liquid hydrogen as determined by a rhodium-platinum resistance thermometer." By James Dewar, LL.D., F.R.S.

The difficulties in liquefying hydrogen caused by the presence of air in the gas have been referred to (*Proc.*, 1898, 14, 130), and later experiments have had for their object the removal of this fruitful source of trouble. This is by no means easy, as quantities amounting to only a fraction of a per cent. accumulate in the solid state, and eventually choke the nozzle of the apparatus, necessitating the abandonment of the operation. Within the last week, the author had succeeded in obtaining 250 c.c. of colourless liquid hydrogen, and this had been employed in a re-determination of the boiling point. Earlier observations (*ibid.*, 146), made with a pure platinum resistance thermometer, had given $-238°$ as the boiling point, and a new thermometer, constructed from pure platinum from a different source, gave practically the same result. As this might be affected by some constant error, the determination was checked by employing a thermometer constructed from an alloy of rhodium and platinum, containing 10 per cent. of the former. Alloys had been shown by Professor Fleming and the author to differ from pure metals in showing no sign of becoming perfect conductors at the absolute zero of temperature, and a study of the rhodium-platinum alloy had shown that the change in conductivity produced by cooling from 0° to the boiling point of liquid air is regular, and may be represented by a straight line. As determined by the rhodium-platinum thermometer, the boiling point of hydrogen was found to be $-246°$. Two ways of explaining the discrepancy between the two determinations suggested themselves. Pure platinum, although its resistance may be represented by a straight line almost down to the solidifying point of air, shows signs of a departure from regularity at about this point, and the curve may become asymptotic at lower temperatures. On the other hand, the resistance of the rhodium-platinum alloy diminishes less rapidly at these lower temperatures and is much higher than that of pure platinum under similar conditions. It follows that its resistance-temperature curve, in all probability, deviates less from a straight line than is the case with platinum. Either cause would explain the differences observed, but the lower boiling point, $-246°$, or 27° absolute, seemed to be the more probable, as it agreed very fairly with the value for the boiling point calcu-

lated by the author from Wroblewski's results and that arrived at by Olszewski. As the use of other pure metals or alloys could not lead to more satisfactory results, the problem must be attacked in a different way by means of an "air" thermometer containing hydrogen under diminished pressure.

Addendum, March, 17th, 1899.—Since this paper was communicated, the author has made a first attempt at determining the boiling point by a constant volume hydrogen thermometer working under diminished pressure. The result is that this thermometer, which gave the boiling point of oxygen as 90·5° absolute or −182·5°, gave for hydrogen 21° absolute or −252°. The three determinations that have been made are then as follows: (1) pure platinum resistance thermometer, 35° absolute; (2) rhodium-platinum resistance thermometer, 27° absolute; (3) Hydrogen thermometer, 20° absolute. From this it appears that the boiling point of hydrogen is really lower than was anticipated. The experiment will be repeated with thermometers filled with hydrogen prepared from different sources. The boiling point should be determined by the use of a hydrogen thermometer filled with gas obtained from the evaporation of the liquid hydrogen itself.

***43. "Influence of substitution on specific rotation in the bornylamine series." By M. O. Forster, Ph.D., B.Sc.**

Certain alkyl derivatives of bornylamine have been prepared, in order to ascertain the effect produced by substitution on the specific rotatory power of the base. The following observations have been made:—

1. The specific rotation of bornylamine is largely increased by the replacement of a single hydrogen atom in the amino-group by an alkyl radicle.

2. In ascending the homologous series of monalkyl derivatives, a maximum specific rotation occurs at the ethylic term; if the molecular rotation is considered, the maximum appears at the propylic term.

3. A maximum specific and molecular rotation, occurring at the ethylic term, is also met with in the two series comprising the hydriodides and the benzoyl derivatives of the homologous bases.

4. The specific rotation of bornylamine is slightly increased on replacing both hydrogen atoms in the amino-group by alkyl radicles, but the magnitude of this increase is inconsiderable when compared with that produced by substituting an alkyl radicle for a single atom of hydrogen.

5. The specific rotatory power of paranitrobenzylbornylamine approximates more closely to that of benzylbornylamine than does that of the orthonitro-compound, but this does not apply to the molecular rotation.

6. When an alkyl group replaces hydrogen of the ammonium radicle in the series of alkylbornylammonium iodides, the specific rotatory power of bornylamine hydriodide, instead of undergoing increase in the positive direction, becomes reduced to feeble lævorotation.

7. The monalkylbornylamines, although strongly dextrorotatory, give rise to benzoyl derivatives which are strongly lævorotatory.

The following bases have been prepared and examined. *Methylbornylamine, dimethylbornylamine, ethylbornylamine, diethylbornylamine, normal propylbornylamine, isopropylbornylamine, butylbornylamine, benzylbornylamine, orthonitrobenzylbornylamine, and paranitrobenzylbornylamine.* Certain salts of these compounds have been also characterised.

Discussion.

Dr. Armstrong said that mere simple relations of mass were by no means the sole controlling influences in the case of other properties, and it would be surprising had optical activity been found to be an exception to the rule. In all experiments on optically active compounds, it was difficult to discount the effect of association which, as other workers in the field had suggested, might afford an explanation of divergencies in a series of homologues such as those recorded by the author. The marked differences in the rotatory powers of the alkyl- as compared with the dialkyl-bornylamines, was only an additional illustration of the fact that asymmetry has an influence entirely different from that of symmetry on the properties of substances.

Dr. Lewkowitsch suggested that interesting results would be obtained if the author were able to prepare a homologue of dimethylbornylamine methiodide in which the two methyl groups were replaced by two different alkyl groups of greater mass, say, by propyl and butyl respectively. The nitrogen would thus become asymmetric, and as, from Le Bel's experiments (*Compt. rend.*, 1890, **110**, 144), it might be expected that optical activity would ensue, the examination of a product containing asymmetric carbon and nitrogen atoms could not fail to give important results.

Dr. Crossley remarked that the curious behaviour of the isopropyl group, referred to by the author, was not at all uncommon in the case of ethereal salts of substituted malonic acids. For example, α-ethyl- and *aa'*-methylethyl-pimelic acids could be prepared by the interaction of the ethereal salts of corresponding substituted malonic acids with trimethylene chlorobromide (*Trans.*, 1894, **65**, 987), but similar experiments made with the object of preparing methylisopropylpimelic acid had not given satisfactory results, and up to the present had not been completed. Another example was to be found in the preparation of ethylisopropylacetic acid from the corresponding malonate, the introduction of the isopropyl group being attended

with great difficulty. It would be of interest to know what was the effect on the rotatory power of substituting dissimilar alkyl radicles in bornylamine.

Dr. FORSTER, in reply, stated that practical difficulties had hitherto prevented the examination of the derivatives of bornylamine to which Drs. Lewkowitsch and Crossley had referred. It had not been possible to prepare by direct methods either unsymmetrical alkylbornylammonium iodides or dialkylbornylamines, but this object had been kept in view, and an attempt would be made to deal with the question at some future time.

***44. "Contribution to the characterisation of racemic compounds." By A. Ladenburg, For. Mem. C.S.**

The author refers to the fact that his definition of racemism has not received confirmation from the experiments of Kipping and Pope, but believes that the principle involved in it is correct and has only been expressed in a misleading manner. He therefore substitutes the following: To characterise an inactive substance, determine its solubility with and without the addition of one or other of its optically active components at the same temperature and with the same solvent. If the solubilities are different, the substance is a racemic compound, if the same, it is an enantiomorphous mixture. Experiments with racemic acid, *i*-pyrotartaric acid, and an inactive mixture of sodium ammonium *d*- and *l*-tartrates are given in support of this view.

DISCUSSION.

Mr. W. J. POPE said he was gratified to learn that Professor Ladenburg agreed with the criticism passed by Kipping and himself (*Trans.*, 1899, **75**, 36) upon the older work respecting the characterisation of racemic compounds. The amended form into which Professor Ladenburg cast his statement was not, however, identical in principle with the older one, as the two statements involved absolutely different principles. The older statement said that the solution of a non-racemic optically active mixture of antipodes should deposit, on crystallisation, a mixture of the antipodes of the same composition as that in solution; this view Kipping and he had shown to be untenable. Professor Ladenburg's new statement was quite independent of any similarity of composition between the mixture in the solution and that in contact with the solution; it merely embodied the principle which Kipping and he had stated and shown to be true by experiments on mixtures of sodium ammonium dextro- and lævo-tartrates, namely, that the most soluble non-racemic mixture of two enantiomorphously related substances is a mixture in equal proportions. The facts (*a*) that a racemic compound had a different solubility alone than when mixed with one of its enantiomorphous constituents, and (*b*) that an

inactive non-racemic mixture of two antipodes had the same solubility as a mixture containing excess of one constituent, were simple consequences of the phase rule. In case (*a*), the solution in equilibrium with the racemic compound was saturated with respect to a single substance only, but on adding one of the active components, the solution became either saturated with respect to two substances—the racemic and the active—or saturated with regard to the racemic substance and partially saturated with respect to the active substance; in either case, as Professor Ladenburg found with the tartaric and pyrotartaric acids, the solution changed in concentration. In case (*b*), the solution in equilibrium with, and in contact with, the non-racemic inactive mixture was saturated with respect to both *d*- and *l*-constituents, and addition of excess of one solid constituent did not affect the mixture going into solution, because it did not alter the solid phases in contact with the solution. Thus Professor Ladenburg found the solubility of a compensated mixture of sodium ammonium *d*- and *l*-tartrate to be the same as that of non-compensated mixtures; from the work of Kipping and himself, it was to be premised, not only that the solutions were in both cases equally concentrated, but were both inactive, containing equal quantities of the *d*- and *l*-isomerides. He could not agree with the view that Professor Ladenburg's experiments proved that "ammonium sodium *d*- and *l*-tartrate remain uncombined in the solution"; the experiments proved merely that the *d*- and *l*-salt in contact with the solution were uncombined, but threw no light on the condition of the dissolved material. Professor Ladenburg's new statement was indisputable; it was corroborated by the work of Kipping and himself, and had nothing in common with his older definition of racemism.

Dr. Lewkowitsch suggested that the examination of a racemic compound which was more soluble in water than its optical isomerides would complement in some way the results obtained with racemic acid, which was less soluble than either dextro- or lævo-tartaric acid.

45. "Rotatory powers of optically active methoxy- and ethoxy-propionic acids prepared from active lactic acid." By Thomas Purdie, F.R.S., and James C. Irvine, B.Sc.

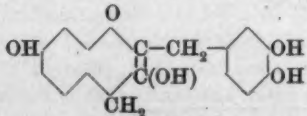
The authors have applied the method of alkylating the ethereal salts of hydroxy-acids by means of alkyl iodides and silver oxide (*Trans.*, 1899, **75**, 157) to lævorotatory methylic and ethylic lactates, and have obtained methylic methoxypropionate and ethylic ethoxypropionate, the specific rotations of which at 20° were found to be $-95{\cdot}53°$ and $-79{\cdot}69°$ respectively. These high values, and the fact that the rotations are of the same sign as that of the lactates, confirm the conclusion that the alkyl lactates made from the silver salt owe their high activity to the presence of small quantities of alkyloxypropionates.

Anhydrous methoxy- and ethoxy-propionic acids, as well as ethylic methoxy- and methylic ethoxy-propionates, were prepared; the molecular rotations of the anhydrous acids were about equal to one another, and those of the methoxypropionates higher than those of the corresponding ethoxy-compounds; a result which seemed to be at variance with previous observations (*Trans.*, 1898, 73, 862) on the metallic salts of the same acids otherwise obtained, according to which the methoxypropionates were the less active. The molecular rotations of the metallic salts of the two acids obtained as above, however, confirm the previous observations. Curves representing the decrease of rotation with increasing concentration show that the factor causing the decrease has a greater effect on the methoxy- than on the ethoxy-salts, and that the difference is more marked in the case of the salts of divalent metals.

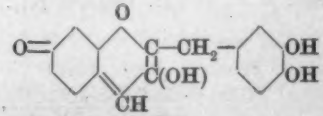
The rotations of the acids in aqueous solution are less than in the anhydrous state, and are nearly constant on dilution, that of the methoxy-acid, as in the case of the ethereal salts, being the higher. It seems probable that the anhydrous acids contain molecular aggregates of higher activity than the individual molecules or ions, and that the higher activity of the methoxy-acid in aqueous solution, as compared with the ethoxy-acid, is due to the acid, like the salts, being more influenced by this factor.

46. "On Brasilin and Hæmatoxylin. II." By A. W. Gilbody and W. H. Perkin, jun.

In continuing their investigations on the constitution of these substances, the authors oxidised dimethylbrasilin with permanganate, and obtained in this way an acid melting at 173°, which, on analysis, gave numbers agreeing with those required for the formula $C_{10}H_{10}O_6$. This acid is dibasic, the silver salt having the formula $C_{10}H_8Ag_2O_6$; it is characterised by great stability, permanganate only attacking it with difficulty at 100°; it gives no coloration with ferric chloride, but when fused with potash, and the acidified product extracted with ether, a substance is obtained which gives with ferric chloride an intense violet coloration, and is, therefore, probably resorcinol, or one of its derivatives. After a careful study of the various new oxidation products described in their previous communication (this vol., 27), the authors conclude that brasilin and brasilein are probably represented by the formulæ :—



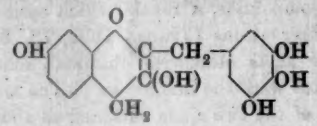
Brasilin.



Brasilein.

but they must reserve for the detailed paper the reasons which have led them to this conclusion.

If the formula for brasilin should prove to be correct, the constitution of hæmatoxylin will probably be represented by the formula:—



from which a formula for hæmatein similar to that assigned to brasilein can readily be deduced.

47. "Crystallisation of dynamic isomerides. A correction." By T. M. Lowry, B.Sc.

In his paper on "Nitrocamphor as an Example of Dynamic Isomerism," the author states (*Trans.*, 1899, **75**, 231) that the laws governing the crystallisation of isodynamic substances had not yet been discussed, and the behaviour of nitrocamphor and π-bromonitrocamphor on crystallisation is used as a basis for the theoretical treatment of the subject. A paper by Roozeboom, entitled "Ueber die Erstarrung flüssiger Mischungen tautomerer Stoffe," which has just appeared (*Zeit. physikal. Chem.*, 1899, **28**, 289), has drawn the author's attention to the fact that he had unfortunately overlooked the full theoretical discussion of the subject by Bancroft in two papers on "The Equilibria of Stereoisomers" (*J. Physical Chem.*, 1898, **2**, 143, 245). The behaviour of nitrocamphor and π-bromonitrocamphor, and the conclusions arrived at from the study of these two special cases, are completely in accord with the general laws deduced by Bancroft.

ANNIVERSARY MEETING.

The Anniversary Meeting will be held on Wednesday, March 29th, *at 3 o'clock in the afternoon.*

At the next ordinary meeting, on Thursday, April 20th, the following paper will be communicated:—

"On some dipyridine derivatives from citrazinic acid." By W. J. Sell, M.A., and H. Jackson, B.A., B.Sc.

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PROCEEDINGS
OF THE
CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 15. No. 207.

March 29th, 1899. Anniversary Meeting. Professor Dewar, F.R.S., President, in the Chair.

Dr. E. W. Voelcker and Mr. W. P. Bloxam were appointed Scrutators, and a ballot was opened for the election of Officers and Council for the ensuing year, the ballot being closed at the conclusion of the President's address.

The PRESIDENT, in beginning his address, said that the past two years had been marked by change in the ranks of the active officers of the Society. Last year, Professor Thomson, who had been an Honorary Secretary since March, 1883, resigned office. His services to the Society had been beyond praise, not only from the amount of work actually done, of forethought and care expended, but also from the personal influence which enabled him to discharge the often delicate duties of his office without wounding the susceptibilities of those with whom he had to deal. Dr. Wynne, who became Junior Secretary last year, had now resigned the post to take up the arduous duties of Editor of the Society's Journal. Dr. Thorpe, who had been honorary Treasurer since 1889, vacated the office that day, the eminent services which he has rendered, not only to Chemical Science, but to the Society, recommending him to the Council for the highest honour the Society had to bestow. Dr. Tilden, who had served the Society twice as Vice-President, would succeed him as Treasurer, and Dr. Scott had been nominated to succeed Dr. Wynne as Secretary. The names of these gentlemen were familiar to the Society as those of persons in every way qualified to discharge the duties of their respective offices.

The Treasurer, as he might still for some minutes call him, would no doubt render them an account of his stewardship, but the duty was incumbent upon him of expressing their deep sense of the debt of gratitude owed him by the Society. During 10 years of office, despite the magnificent undertakings of which Dr. Thorpe had been the mainstay, the investments of the Society had increased by one-half, and its income had risen from £4150 to £5286, while, largely

owing to his vigilant care, the tendency to an increased expenditure had been kept down to normal proportions.

During his term of office he had had to provide the funds for some very considerable undertakings, chief amongst which were the alterations effected in the meeting room and the introduction of the electric light in 1892, the Society's Jubilee in 1891, and the drawing up of General Indexes to the Society's Journal and the Abstracts from 1873 to 1892. On the completion of this latter piece of work, which Dr. Thorpe would announce to the meeting, it seemed a fitting time to acknowledge the service which the publication of these volumes has rendered to every one interested in the science. They had been issued gratuitously to all Fellows who had received the Journal during the period they cover, provided that application was made for them before December, 1895.

Though the initiative in this issue had been taken by our illustrious colleague, the main burden of the preparation of the Index had fallen on a lady, Mrs. Dougal, who edited the two volumes with zeal, energy, and intelligence. He (the President) would wish to bear testimony to her self-sacrificing devotion to this task, which had occupied upwards of five years. It had proved to be one of uncommon and unexpected difficulty. The annual indexing was found to have been done in an irregular and unsystematic way in the past, and much of the work which was understood to be ready to her hand had to be done over again. She had, both directly and indirectly, done the Society a great service—directly, by the compilation which she had executed, and indirectly, by leaving an example of thoroughness and accuracy to her successors. He had also to tender their thanks to the ladies who assisted her, and to Miss Neale, who had taken her place for a short time. The thanks of the Society were also due to the Index Committee, and more especially to Dr. Forster Morley, whose unwearied assistance and experience did much to solve the problems which were daily met with in the progress of the work.

The yearly indexes to the Journals had of late shown a tendency to expansion. With a view to making them of more service, a staff of Indexers, having a special knowledge of the various departments they undertook, had been engaged.

During the past year the Society was privileged to offer to six of its Past-Presidents its congratulations, and those of the whole Scientific world, on the occasion of their completing fifty years' Fellowship of the Society. The Banquet at which they were entertained would long live in their memory. To quote the words of Friedel, "No finer phalanx of the Fathers of our Science exists in any country." The occasion was too recent for him to add anything to the sentiments then expressed. The event, however, was not without a melancholy

side. As originally proposed, the foremost of this phalanx would have been their senior Past-President, the last surviving Founder of the Society. He would not speak here at length of the services Lord Playfair had rendered to Science, but fifty years' active work in the service of the Society required a more special mention. He became a Member of the Council in 1846, in 1850 he was elected a Vice-President, in 1857 he became President of the Society in succession to Professor Miller, and from 1859, for forty years, he remained Vice-President of the Society to which his experience and influence rendered signal service. His last appearance amongst them had been to propose him (Prof. Dewar) as President.

During the past two years, the Society had lost by death thirty-six of its Fellows. Lord Playfair was the last survivor of the seventy-seven original members of our Society. In Mr. J. W. Rodger, the Society lost one of the most promising of the younger men of science and a Member of its Council. Sir Thomas Dyke Acland had been a Fellow of the Society for over forty years, and though he had never taken an active part in the affairs of the Society, he had rendered great services to our Science in its connection with Agriculture. Sir Douglas Galton, whose recent loss they had to deplore, had been a Fellow of the Society for a quarter of a century. Mr. Newlands, whose "Law of octaves" has taken an imperishable place in the history of Science, was in his fortieth year of membership, and had also served the Society as a Member of Council. His portrait now occupied a place on their walls.

Mr. Groves, who had been connected with the Journal since 1878, first as Sub-Editor, and, in 1884, as Editor in succession to Mr. Watts, resigned office that day. Only those who have been connected with similar publications could measure the full extent of the Society's indebtedness to him, but they could all join the Council in expressing their deep sense of, and thanks for, the important services he had rendered to the Society during those twenty-one years. They could only express the hope that his work for the Society and for Science might be continued for many years to come.

Mr. Greenaway, who had for so many years occupied the important office of Sub-Editor, and worked so harmoniously with Mr. Groves, had elected to remain in that position. Dr. Wynne had succeeded Mr. Groves in the editorial chair and could be trusted to preserve that high level of excellence to which the Society's Journal had attained.

The number of papers read before the Society during the past two years was 274, of which 216 had since been published in full in the Society's *Transactions*, the remaining papers being preliminary notices of a more or less temporary character.

The Meetings of the Society had been well attended, and the

discussions fruitful of interest, but he could desire, in the best interests of the Society, that a larger proportion of the senior Members could find it possible to be present.

During the past two years considerable attention had been given by the Council to the question of a suggested revision of the Bye-Laws. It has been found that no important modification can be made in these without the grant of a new Charter, and it is thought that it is hardly worth while to introduce mere verbal changes which might, perhaps, make the meaning of the Bye-Laws more clear, but which, the Council is legally advised, are unnecessary in view of the established practice of the Society.

The next matter of importance which would engage the attention of the Society would probably be the issue of a new catalogue to the Society's Library. Originally founded in 1850, it then consisted of about 270 volumes of journals, 60 miscellaneous volumes, and 100 pamphlets. Its first catalogue was issued in 1851, a second catalogue was prepared by Mr. Watts and issued early in 1861, a third catalogue, now grown from 28 to 112 pages, was issued in 1869, and a fourth, of 138 pages, in 1874. In 1886, a new catalogue, arranged according to subject matter was drawn up by Mr. Warington from Mr. Watts' notes, and issued to the Society. It extends to 327 pages, and has an Author-index drawn up by Professor McLeod. The catalogue of 1886 contains entries of 5580 volumes of journals, 4223 books, and 1380 pamphlets. Since that time there have been added 3279 volumes of journals, 1361 books, and over 1600 pamphlets. The preparation and issue of this important work would necessarily involve some considerable time and expense to the Society.

One of the great needs of scientific workers is a ready means of acquainting themselves with the bearing and results of general scientific work. The publication of Abstracts of particular branches of science is, generally speaking, nearly complete, but there is great overlapping and waste of energy. The suggestion has been made that some change analogous to that recently carried out by the German Chemical Society should be made in the publication of our own Abstracts. All such proposals will have the fullest consideration of the Council, but it is clear that it would be unwise to ignore the grave consequences to the financial position of the Society which might result from any too precipitate change in the method of publication of the Abstracts. Without entering more fully on this question, he might remark that there was still room for co-operation in this matter between the societies of this country.

They had been asked to co-operate with the American and the German Chemical Society in bringing about an International agree-

ment upon the subject of Atomic Weights. The Council has appointed a Committee to consider the matter.

In the meantime, they had had the opportunity of co-operating in the movements designed to honour the memory of two illustrious chemists, Kekulé and Davy; the former by joining in the International Memorial to his memory, the latter by contributing, in conjunction with the Royal Institution and the Royal Society, to a fund designed to restore and preserve the memorial raised over his grave.

The remainder of the address was of a general and theoretical nature, dealing with recent advances in Chemical research, principally in connection with low temperatures.

The numerical strength of the Society was as follows :—

Number of Fellows, March 31st, 1898		2140
,, ,, since elected		132
,, ,, reinstated by Council		3
		2275
Removed on account of non-payment of two annual subscriptions	15	
Withdrawn	12	
Deaths	18	45
Number of Fellows, March 31st, 1899		2230
Foreign Members		38

The names of those removed were:—E. S. Cameron; F. E. J. Cridland; F. W. S. Glenfield; E. Hawkins; L. W. Hawkins; A. J. Heath; W. Hesketh; H. Heywood; J. Hulme; F. Ibbotson; J. E. W. McFall; T. A. Reid; B. E. Smith; J. H. Starling; F. H. Wigham.

The following have withdrawn :—Bennett F. Davenport; Henry Winram Dickinson; Arnold Eiloart; K. S. Engineer; C. H. Reissman; A. G. Scorer; Bomanji Sorabji; Walter J. Sykes; William Gilchrist White; John Williams; W. M. Wilson; B. Winstone.

The following have died :—Sir T. J. Dyke Acland; W. R. Burnett; Michael Conroy; E. Rider Cook; Ramchandra Dutta; George Foord; Sir Douglas Galton; Jeremiah Head; J. G. Heywood; W. L. Hiepe; Charles Lowe; J. A. R. Newlands; Eugen Obach; Lord Playfair; Manning Prentice; H. W. Seely; Matthew Smith; Samuel Spencer.

The number of communications made to the Society during the year was 150.

One hundred and two papers were published in the *Transactions*

for 1898, occupying 1047 pages, whereas in the preceding year 114 papers were published, occupying 1204 pages.

The following were the statistics relating to the Abstracts.

PART I.

	Pages.	No. of Abstracts.
Organic Chemistry	720	1187

PART II.

General and Physical Chemistry		344
Inorganic Chemistry		284
Mineralogical Chemistry		171
Physiological Chemistry		165
Chemistry of Vegetable Physiology and Agriculture		159
Analytical Chemistry		516
	660	1639
Total in Parts I. and II.	1380	2826

Seven hundred and twenty-seven volumes had been borrowed from the Library. The additions comprised 67 books, 285 volumes of periodicals, and 24 pamphlets.

Dr. GLADSTONE, F.R.S., proposed a vote of thanks to the President, coupled with the request that he would allow his address to be printed in the *Transactions*.

Dr. ARMSTRONG, F.R.S., seconded the motion, which was carried by acclamation.

The PRESIDENT having returned thanks,

Dr. THORPE, F.R.S., the Treasurer, in giving an account of the Balance Sheet which he laid before the Society, duly audited, said:—

The receipts had been:—By admission fees and subscriptions, £4064; by sale of Journal and advertisements, £740 15*s.*; and by dividends on invested capital, £428 2*s.* 1*d.* The expenses had been:—On account of the Journal, £3007 9*s.* 10*d.*; on account of the Proceedings, £287 6*s.* 10*d.*; on account of the General Index, £793 16*s.* 7*d.*; on account of the Library, £294 19*s.* 11*d.*; House expenses, £238 2*s.* 7*d.*; the total expenditure being £5415 6*s.* 8*d.* Grants amounting to £245 had been made to Fellows from the Research Fund during the year, and a sum of £1316 1*s.* had been invested in the purchase of £1400 India 2½ per cent. Stock.

On laying down his office as Treasurer, to which he was elected in

1889, Dr Thorpe hoped that it might not be uninteresting to the Fellows if he gave a brief account of the financial progress of the Society during the ten years of his stewardship.

In 1889, the total assets of the Society, excluding the Research Fund, were £12,221; in 1899 they are £17,289.

The total assets of the Research Fund in 1889 were £5464; in 1899 they are £7618.

The aggregate total assets are now £24,907, as against £17,686 in 1889.

In 1889, the total receipts from Fellows were £3402; in 1899 they are £4064, or an increase of 19½ per cent. The annual income from the sale of the Society's publications in 1889 amounted to £365; this year, including an outstanding item on account of advertisements, it is £760, or an increase of 108 per cent. This is due partly to the increased circulation of the Journal and partly to the increased price which can be obtained for it. The advertisements now bring in an income equivalent to about £2000 of funded property.

The total income of the Society from all sources in 1889 including the balances at the Bank was £5824; at the close of the present financial year it has amounted to £7180.

It will be seen, therefore, that whilst the receipts from the Fellows have increased by 19½ per cent., the income of the Society has increased by 23·3 per cent., and the total assets, some of which may be counted upon to still further increase the annual income, have increased by 40·8 per cent.

But if it may be said of Societies, as of individuals, that their riches consist, not in the abundance of their possessions, but in the fewness of their wants, it is the experience of the Treasurer that the Chemical Society is by no means a rich corporation, for its wants advance, almost *pari passu*, with its possessions. His successor would find that, however ingenious he may be in securing money, the Society, with equal or with even greater ingenuity, will find a method of relieving him of it.

He regretted to find that he had—he hastened to add, by direction of the Council—signed cheques for a greater amount than any one of his predecessors. During the ten years he had been in office he had disbursed nearly £45,000 of the Society's money. In explanation of this, he might point out that the annual cost to the Society of its publications has steadily increased since 1889. In that year, the expenses connected with its publications came to £2565; this year, in spite of a considerable saving in the printer's bills, and in spite of the draconian methods of the Publication Committee, its publications, excluding the Collective Index, have cost £3370.

The expenses on account of the Library also steadily increase. In 1889, £196 was spent in books, periodicals, and binding; this year, which has been somewhat below the average of the preceding years, the amount has been £246.

The House expenses in 1889 came to £184; this year they are £238.

The total expenditure in 1889 was £3430; this year it has been £5415.

As regards these disbursements, he might be pardoned, perhaps, for pointing out that none of his predecessors had been called upon to spend so large an amount of the Society's money in what might be termed extraordinary expenditure. To begin with, his immediate predecessor handed him over—and it was his only legacy—certain applications for increase of salary on the part of the Editorial staff, and he was good enough to urge that he should deal with them liberally. The liberality has resulted in a difference of £1000 to the Society.

In 1891, the Society celebrated its Jubilee at a cost, notwithstanding the generous assistance of the Goldsmiths' Company, of about £450. In the following year, the alteration of the Meeting Room and the installation of the electric light was taken in hand, at a cost of £1490.

Shortly afterwards, the Society was called upon to provide for the declining years of an old and faithful servant. There was no circumstance connected with his official career as the Treasurer of the Society which he recalled with greater pleasure than its action in regard to Mr. Josiah Hall's pension.

In the early part of 1894, the Society determined to print a Collective Index of its publications from 1873 to 1892. This has proved to be even a more formidable undertaking than was expected. It has occupied nearly five years in execution, and has cost some £1740. It is now happily completed, and the Society may congratulate itself upon possessing an adequate key to the great store of chemical knowledge which it has accumulated during twenty years.

The revision of the Annual Indexes necessitated by this great work has shown the absolute need for their more systematic preparation. This has led to the establishment of a special staff of indexers, at an annual cost to the Society of upwards of £60.

Another item of expenditure which had arisen during his tenure of office is connected with the lectures which are given in memory of the deceased Foreign Members. The Society has now a collection of eight of these Memorial Lectures, all of which have been given gratuitously by Fellows or friends on the invitation of the Council. Their publication has cost about £400. These lectures together constitute a most valuable record of contemporary chemical history, and it is hoped that, as the

Council have directed, they may be issued in a separate volume, with the accompanying illustrations, before the end of the next financial year.

In their donations to funds connected with the illustrious names of Lavoisier, Davy, Stas, Kekulé, Cannizzaro, the Fellows have not been unmindful of their obligations to these great pioneers in chemical enquiry, nor have they been forgetful, as the gathering of last November showed, of their obligations to the pioneers in their own Society happily still amongst us.

The Account books of the Society show that what he had called the extraordinary expenditure which has been incurred during the last ten years is close upon £7000.

He thought, however, they would all feel that, in the enhanced position of their Society, in the greater comfort and convenience of their Meeting Room, in the improvement and increased value of their publications, they had had an abundant return for this expenditure. Although but for it he might have been able to add a few more thousand pounds to their capital account. He hoped the Fellows would not hold him responsible for this omission, but look with a lenient eye upon the financial transgressions of what he sometimes felt himself to have been—a too compliant purse-bearer.

Mr. DAVID HOWARD proposed that the thanks of the Fellows be tendered to the Treasurer for his services during the past year; this motion was seconded by Mr. F. J. M. PAGE, and carried.

The TREASURER, in responding, proposed a vote of thanks to the auditors.

Prof. HODGKINSON seconded the motion, which was unanimously adopted, and acknowledged by Prof. TILDEN on behalf of Dr. HORACE BROWN.

Dr. E. W. VOELCKER proposed a vote of thanks to the Officers and Council.

Mr. H. B. BAKER seconded the motion, which was unanimously adopted.

Prof. DUNSTAN, F.R.S., responded on behalf of the Council.

Prof. THOMSON, F.R.S., proposed a vote of thanks to the Editor, Sub-Editor, Abstractors, and Indexers, which was seconded by Dr. MESSEL and carried.

Mr. GROVES, F.R.S., responded.

The Scrutators having presented their report to the President, he declared that the following had been duly elected:—

President: T. E. Thorpe, Ph.D., D.Sc., LL.D., F.R.S.

Vice-Presidents who have filled the office of President: Sir F. A. Abel, Bart., K.C.B., D.C.L., F.R.S.; H. E. Armstrong, Ph.D., LL.D., F.R.S.;

A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir W. Crookes, F.R.S.; James Dewar, M.A., LL.D., F.R.S.; Sir E. Frankland, K.C.B., D.C.L., F.R.S.; Sir J. H. Gilbert, Ph.D., LL.D., F.R.S.; J. H. Gladstone, Ph.D., D.Sc., F.R.S.; A. Vernon Harcourt, M.A., D.C.L., F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, LL.D., Ph.D., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., V.P.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents: C. E. Groves, F.R.S.; G. D. Liveing, M.A., D.Sc., F.R.S.; T. Purdie, Ph.D., F.R.S.; William Ramsay, Ph.D., LL.D., F.R.S.; J. Emerson Reynolds, M.D., D.Sc., F.R.S.; John M. Thomson, F.R.S.

Secretaries: Wyndham R. Dunstan, M.A., F.R.S.; A. Scott, M.A., D.Sc., F.R.S.

Foreign Secretary: Raphael Meldola, F.R.S.

Treasurer: William A. Tilden, D.Sc., F.R.S.

Other Members of Council: H. Brereton Baker, M.A.; E. J. Bevan; Frank Clowes, D.Sc.; H. J. H. Fenton, M.A.; W. Gowland; C. T. Heycock, M.A., F.R.S.; D. Howard; Rudolph Messel, Ph.D.; G. T. Moody, D.Sc.; H. Forster Morley, M.A., D.Sc.; Arthur Smithells, B.Sc.; James Walker, D.Sc.

At the next ordinary meeting, on Thursday, April 20th, the following papers will be communicated:—

"Some dipyridyl derivatives from citrazinic acid." By W. J. Sell, M.A., and H. Jackson, B.A., B.Sc.

"The synthesis and preparation of terebic and terpenylic acids." By W. Trevor Lawrence.

"The allotropic modifications of phosphorus." By D. L. Chapman.

"β-Isopropyl glutaric acid." By F. H. Howles, and J. F. Thorpe.

"Ethyl ammonium sulphite." By Edward Divers and Masataka Ogawa.

"Ethyl ammonium selenite and non-existence of amidoselenites (selenosamates)." By Edward Divers and Seihachi Hada.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

The following Candidates have been proposed for election. A ballot will be held on Thursday, May 4th.

Allworthy, James Herbert,
Laxton School, Oundle.

Schoolmaster. Eight years' experience as a teacher of Practical Chemistry. Practical work at University Tutorial College, and Theoretical work in connection with University Correspondence College.

Alfred J. Wilcox. Willie Briggs.
H. O. Hale. George Ryce.
W. J. Lewis.

Auchinachie, Peter,
12, Mid Street, Keith, N.B., *pro. tem.*; 70, Newman Street, Oxford Street, W.

Analytical Chemist. Have passed the Minor and Major Examinations of the Pharmaceutical Society of Great Britain, the subjects being Elementary and Advanced Chemistry (Organic and Inorganic), Materia Medica, Botany, and Physics. Have served as assistant under Mr. C. H. Cribb, B.Sc., F.I.C., F.C.S., Public Analyst to the Strand District, for 2 years. I am now in Analytical practice on my own account.

Cecil H. Cribb. M. Carteighe.
George T. Holloway. *John Wilson.*
Percy F. Frankland. *Charles J. S. Makin.*

Baker, Clement Harrison,
Athelney, Featherstone Road, King's Heath, Birmingham.

Assayer and Refiner. Assayer and Refiner to Messrs. Charles

Harrold and Co., assayers, bullion dealers and refiners, St. Paul's Square, Birmingham. Assayer to The Mint, Birmingham, Ltd.

Chas. Bayliss. Thomas J. Underhill.
H. S. Shorthouse. *W. J. Lancaster.*
Colin Gordon.

Beale, Frederick James,
Wilderspool Brewery, Warrington.

Assistant Brewer and Analyst to Messrs. Greenall, Whitley & Co., Limited, Wilderspool. Studied General Chemistry 10 years under Dr. Cook, F.I.C., F.C.S., Dr. Leicester, F.I.C., F.C.S. One year Technical Brewing Chemistry under J. Heron, Esq., F.I.C., F.C.S., and hold an Advanced Certificate for Practical Inorganic Chemistry, Science and Art Department.

Ernest H. Cook. W. B. Roberts.
James Leicester. *Alex. R. Miller.*
Fred. R. Stone.

Belton, Frank,
103, Lower Seedley Road, Pendleton, Manchester.

Lecturer in Chemistry in the School of Science, Central Higher Grade Scholarship School, Salford, for 5 years. I. First Class, Advanced Stage, in the Examinations of the S. and A. Dept., South Kensington, in Inorganic Chemistry (Theoretical and Practical). II. The Pass Examination in Chemistry for the London Final B.Sc.

W. B. Hards. R. L. Taylor.
Edgar E. Horwill. Chas. T. F. Watts.
Duncan T. Richards.

Bond, Alfred Ernest,
Princes Chambers, Corporation Street, Birmingham.

Iron and Steel Trade and Analytical work connected therewith. Six years' Laboratory work (3 years in Private Laboratory and 3 years in Chemical and Metallurgical Laboratories at Mason University College); at present Analyst for Messrs. J. C. Abbot and Co.

Percy F. Frankland. W. R. Innes.
Godfrey Melland. C. F. Baker.
Andrew Turnbull.

Bratby, George Smith,
Oak Field, Hale, Bowdon, Cheshire.

Manufacturing Chemist. Student for 4 years in the Chemical Dept. of the Owens College.

H. B. Dixon. D. S. Jerdan.
W. H. Perkin, jun. W. T. Lawrence.
William A. Bone.

Browning, Kendall Colin,

St. John's College, Cambridge.

B.A. (Camb.). Assistant Demonstrator at St. John's College, Cambridge. First Class Natural Science Tripos, Parts I. and II., joint author (with Dr. Ruhemann) of the following papers :—"On the Formation of Ethylic Dihydroxydinicotinate" (*Trans. Chem. Soc.*, 73, 280, 1898), "Additive Compounds of Organic Bases and Unsaturated Esters" (*Trans. Chem. Soc.*, 73, 723, 1898), "On Formation of β-Ketonic Esters" (*Trans. Chem. Soc.*, 73, 727, 1898).

H. Brereton Baker.	F. W. Dootson.
S. Ruhemann.	W. T. N. Spivey.
R. Haliburton Adie.	M. M. Pattison Muir.

Collingridge, William,

Port Sanitary Office, Greenwich, S.E.

Medical Officer of Health, Port of London. M.A., Honours Natural Science Tripos, M.D., LL.M., D.P.H., Cambridge. Have been for many years engaged in chemical and bacteriological examination of water, food, &c., in connection with duties as M.O.H. Port., and take a general interest in chemical science in its relation to medicine and public health, specially with regard to adulteration legislation.

W. H. Corfield.	W. H. Symons.
A. Wynter Blyth.	R. J. Friswell.
Christopher Childs.	*W. J. Russell.*
John Muter.	*Henry E. Armstrong.*

Connell, Robert D.,

38, Chapel Road, Stamford Hill, N.

Analytical Chemist. For eighteen months assistant to T. Fairley, Esq., F.R.S.E., F.I.C., F.C.S., Borough Analyst for Leeds. For two years assistant to E. Riley, Esq., F.I.C., F.C.S., Analyst and Assayer, London. Six months Chief Chemist at the Iron Mines of Elba, Italy, and now Chief Chemist to the firm of W. H. Pearson and Co., analysts and mineral samplers, London. Hold First Class Honours Certificate in Practical Inorganic Chemistry, and also Certificate for Organic Chemistry and Metallurgy from the Science and Art Department.

Thomas Fairley.	B. A. Burrell.
Edw. Riley.	James E. Ferguson.

W. H. Pearson.

Darling, Charles Robert,

12, Nithdale Road, Plumstead, S.E.

Instructor in Chemistry and Physics, Royal Military Academy,

Woolwich. Royal Exhibitioner and Associate Royal College of Science, Dublin. Whitworth Exhibitioner. Sometime Assistant Chemist to the London and North-Western Railway Company, Crewe.

W. R. Hopkinson. Alexander Scott.
W. N. Hartley. *Frederic Jas. M. Page.*
Hugh Ramage. *Leonard Temple Thorne.*
A. J. Greenaway.

Goltz, Harold Francis Carl,
7, Craster Road, Upper Tulse Hill, S.W.

Student. Have been studying Chemistry at the Birkbeck Literary and Scientific Institution since 1894. I intend to become an Analytical Chemist, and am also working for the B.Sc. degree.

John E. Mackenzie. Geo. Stubbs.
J. Woodward. Chas. J. Meads.
Edwd. Jones. Frank Gossling.

Haigh, Percy,
312, Romford Road, Forest Gate, E.

Analytical Chemist. Served the usual professional pupilage to C. Estcourt, Manchester. Chemist to Messrs. Dickens, Pease & Co. Science and Art Examinations. Four First Certificates in Science Subjects. City Guilds Silver Medallist. Cambridge Local Examinations. One First Certificate.

C. Estcourt. J. A. Williamson.
W. Hepworth Collins. *H. Bailey.*
Jas. Gardner. *J. Carter Bell.*
Horatio Ballantyne. *Edward Bevan.*

Hughes, John Elias,
Birchville, Wrexham.

Technical Chemist. Have for several years held the position of Chemist to one of the largest leather manufacturing firms in England. Am a member of the "International Association of Leather Trades Chemists," and have for some years acted as a Teacher of Chemistry.

Alfred Neobard Palmer. Robert Hellon.
Henry R. Procter. *Arthur Smithells.*
Herbert Ingle.

Hunter, Archibald Glen Kidston,
Dunedin, New Zealand.

Public Analyst. Analytical Consulting Chemist to Dunedin City Corporation. Lecturer on Chemistry, Technical Schools. Chemist to

Customs Agricultural Government Departments at Dunedin, New Zealand.

Henry de Mosenthal. Arthur R. Ling.
Otto Hehner. B. E. R. Newlands.
Oscar Guttmann. A. Wynter Blyth.
Wyndham R. Dunstan.

Jones, Lauder William,

University of Chicago, Chicago, Ill., U.S.A.

A.B. Williams College, 1892. Fellow in Chemistry, University of Chicago, 1895—7. Ph.D. University of Chicago, 1897. Assistant in Chemistry, *ibid.*, 1897 to date. Publications:—"On Salts of Nitroparaffins and Acylated Derivatives of Hydroxylamine," *American Chemical Journal*, 20, No. 1.

Albert B. Prescott. Alexander Smith.
J. Bishop Tingle. *James Walker.*
Otis C. Johnson.

Judge, Thomas.

142, Waller Road, New Cross, S.E.

Science Master. B.A. St. John's College, Oxford, with First Class Honours in the School of Natural Science (Chemistry). For nearly two years Science Master of Aske's Hatcham School, New Cross, S.E.

Percy Elford. V. H. Veley.
W. Odling. E. G. J. Hartley.
W. W. Fisher. *William E. Moss.*
D. H. Nagel. *H. L. Bowman.*
H. A. Miers.

Lindsey, Robert William,

22, Hilldrop Crescent, Camden Road, N.

Chemical Manufacturer. Pupil at University College under Professor Ramsay in 1890—1. Student in Analytical and Theoretical Chemistry under Mr. T. A. Ellwood, F.I.C., Mr. W. Watson Will, F.C.S., and Mr. F. A. Hocking, B.Sc. At present engaged in chemical manufacture.

T. A. Ellwood. Harry Garnett.
William Ramsay. W. Watson Will.
Rudolph Messel.

MacLeod, James,

Westhill, Cardross Road, Dumbarton.

Analytical Chemist. Studied Chemistry with Messrs. Wallace, Tatlock, and Clark for two years. Acted as Laboratory Assistant to Dr. Clark for two years. For eight years Chemist to the Glasgow

Corporation's Gas Works, Dalmarnock. Contributed paper on "Photometry" to City Analysts' Society, Glasgow.

John Clark.	Horatio Ballantyne.
R. R. Tatlock.	G. G. Henderson.
Thomas Gray.	*J. A. Williamson.*

McConnell, William,

178, Springfield Road, Glasgow.

Practical Dyer and Chemist. I have had a two years' course of Chemistry in the Glasgow Technical College, and am Chemist and practical Dyer here. I have lectured in the Glasgow Weaving College and at Kilmarnock on dyeing. I have been appointed instructor of a dyeing class now started in the Glasgow Weaving College.

G. G. Henderson.	Matthew A. Parker.
James Robson.	Thomas Gray.

A. Humboldt Sexton.

Morris, Wilfred Walter,

Newtown-St. Boswells, Roxburghshire, N.B.

Assistant (Office and Laboratory) to the Medical Officer of Health for the counties of Roxburghshire and Selkirkshire, and Burgh of Melrose. Eight Certificates in Science from Science and Art Department, South Kensington, including 1st Class (Queen's Prize), Advanced Theoretical Chemistry; 2nd Class Advanced Practical Chemistry, and 1st Class Advanced Hygiene. Have worked for some time in the Laboratory of Mr. M. Dechan, F.I.C., F.C.S., Public Analyst, Hawick. Have contributed papers to the *Sanitary Journal* on "Pollution of Rivers" and "Water Supplies." Lectured on the Chemistry of the Air, &c., and other public health matters. Am generally interested in the application of Chemical Science to Public Health work.

M. Dechan.	Harold Rostron.
E. Haworth.	Charles A. Fogg.

Jno. L. Whiteside.

Panting, Laurence Christopher,

9, Beverley Road, Anerley, S.E.

Demonstrator of Chemistry and Physics at Guy's Hospital. B.A., M.B., B.Ch., Oxon, M.R.C.P., London. Scholar of Balliol College, Oxford. Honours in Final School in Chemistry. Joint author of "Preparation of Hydrogen Cyanide and Carbon Monoxide," *Trans.*, '73, 255, 1898.

Thos. Stevenson.	D. H. Nagel.
Charles E. Groves.	A. Vernon Harcourt.
John Conroy.	John Wade.

Pittuck, Frederick Williams,

19, Stratford Grove, Newcastle-on-Tyne.

Manufacturing Chemist, with considerable experience in the manufacture of barium salts, purification of copper, and extraction of silver therefrom, arsenic, &c., and for several years engaged in commercial analysis (slags, clays, cements, &c.), also assaying lead, silver, and gold.

Thomas Tyrer. Frederick Gilderdale.
J. Fleming Stark. Geo. F. Merson.
A. Garden Hendry. *J. Wilson Swan.*

Read, Harold McLean,

127, Warwick Road, Earls' Court, S.W.

Assistant Chemist in the Research Laboratory of the Imperial Institute. Student in the Pharmaceutical Society's School, 1894—1895. Student in the Pharmaceutical Society's Research Laboratory, 1895—1896.

Wyndham R. Dunstan. H. A. D. Jowett.
J. T. Dunn. R. L. Jenks.
Ernest Goulding.

Schryver, Samuel Barnett, D.Sc. (Lond.), Ph.D. (Leipzig),

27, Arundel Gardens, W.

Chemist. Author of "Researches on Oxidation Products of Turpentine Oil," "Researches on Camphoric Acid," and other papers published by the Society.

Frederick B. Power. W. Palmer Wynne.
H. A. D. Jowett. M. O. Forster.
William Ramsay.

Schweich, Maurice Emile,

85, Belgrave Road, S.W.

Technical Chemist. Student of Chemistry for five years at the Polytechnical School, Zurich, where obtained Diploma for Chemistry, and has been ever since engaged in manufacturing Chemistry.

Ludwig Mond. Joseph W. Swan.
James Dewar. Thomas Tyrer.
Alfred Gordon Salamon.

Shelbourn, Edward Thomas,

1, Chalcot Crescent, Regent's Park Road, and 40, Craven Street, Strand.

Assistant Analyst in L.C.C. Laboratory. Four years' course in Chemistry at University College, Nottingham. Assistant three

years to Dr. A. Hill, City Analyst, Birmingham. Associate of the Institute of Chemistry since 1894. Now F.I.C.

Frank Clowes. J. H. Coste.
Alfred Hill. A. Hunter Boylan.
J. Bernard Coleman. E. Brooke Pike.
R. Grimwood. *R. Bodmer.*
Ernest J. Parry. *J. Wade.*

Shelton, Arthur John,
19, Sturry Street, Poplar, E.

Chemist to Messrs. Fowler, Ltd., Sugar Refiners, Blackwall. Associate of the City Guilds Institute (1896). Late Assistant to John Heron, F.I.C., F.C.S.

Henry E. Armstrong. Gerald T. Moody.
John Heron. A. Lapworth.
Sidney Williamson. W. Palmer Wynne.

Thiersch, Harry Alexander,
8, Clifton Gardens, London, W.

Analytical Chemist. Educated at Wiesbaden and Berne. Studied Chemistry at King's College, London, during the Sessions 1897—1898. Since November, 1898, with Dr. Dupré, F.R.S.

John M. Thomson. A. Dupré.
Herbert Jackson. Patrick H. Kirkaldy.
Leonard M. Nash. S. Dickson.

Thomson, Robert Tatlock,
156, Bath Street, Glasgow.

Analytical Chemist and Public Analyst. Author of various articles on "Indicators in Volumetric Analysis," *Chemical News*, 1883, 1884, and 1885; and *Journal of Society of Chemical Industry*, 1887 and 1893; "On the Analysis of Oils and Fats" *Jour. Soc. Chem. Ind.*, 1890, 1891, and 1892; "On Water for Dietetic Purposes," *J.S.C.I.*, 1894; "On Boric Acid in Foods," *J.S.C.I.*, 1895; "Formic Aldehyde as a Preservative," *Chem. News*, 1895, &c.

R. R. Tatlock. William Ramsay.
Alex. Crum Brown. Edmund J. Mills.
Alfred H. Allen.

Threlfall, Richard,
45, Frederick Road, Edgbaston, Birmingham.

Scientific Director to Messrs. Albright & Wilson, Ltd., Oldbury. Late Professor of Physics, University of Sydney, N.S.W. Papers on Physico-Chemical matters: amongst others, "On the Electric Proper-

ties of Pure Sulphur," *Phil. Trans.*, 1897; "On the Measurement of High Specific Resistances," *Phil. Mag.*, 1886—1889; "On Electric Discharge in Purified Gases," *Phil. Proc.*, 1886, and *Phil. Mag.*, 1891 (?); "On Losses of Energy in Cycles of Electrification of Purified Substances," *Physical Review*, 1897. Books: *Report of N.S.W. Royal Commission on Spontaneous Heating of Coal*, of which the candidate was President. Handbook of *Spontaneous Heating of Coal Cargoes*. N.S.W. Government Publication. *Laboratory Arts*, Macmillan. 1898.

Henry E. Armstrong. M. M. Pattison Muir.
William A. Tilden. Alexander Scott.
Geo. S. Albright.

Tyler, Ernest Albert,
Warsop, Mansfield, Notts.

Science Master, Devon County School, South Molton. B.A., Cambridge. Late Science Scholar, St. John's College, Cambridge, Worked conjointly with Dr. Ruhemann on "Ethylic Acetoacetates," published in the Transactions of the Chemical Society, 1896.

S. Ruhemann. M. M. Pattison Muir.
R. H. Adie. Sidney Skinner.
F. H. Neville.

Wade, Arthur Luvian,
28, West Kensington Gardens, W.

Analytical Chemist. Three years a student with the late Professor R. Fresenius at Wiesbaden. Two years assistant to Martin Dechan, Esq., F.I.C., Public Analyst, Hawick, N.B.

B. E. R. Newlands. Henry Bailey.
Arthur R. Ling. *Oscar Guttmann.*
Otto Hehner. *Henry de Mosenthal.*
Thomas Royle.

Walden, Allan Frederick,
New College, Oxford.

(M.A. Oxon.) Lecturer in Chemistry in New College. Demonstrator in the Balliol College Laboratory. First Class, Final Honour School (Chemistry), 1895.

William Odling. D. H. Nagel.
W. W. Fisher. P. Elford.
John Watts. J. E. Marsh.

Walker, Charles,
Care of T. B. Walker, Scott Chambers, Pitt St., Sydney, N.S.W.

Metallurgical Chemist and Assayer. Three years a Student in the

Chemical, Metallurgical, and Geological Laboratories of the University of Sydney, N.S.W. Two years Geological Assistant to the Mount Morgan Gold M. Co., Ltd., Queensland. Six months Junior Demonstrator of Chemistry, University of Sydney.

A. Liversidge. F. W. Guthrie.
J. A. Schofield. *Wm. A. Dixon.*
William M. Hamlet.

Watson, Fred Sheasby,
Springside, Disley, Cheshire.

Senior Assistant Science Master at the High Pavement, Stanley Road Board Higher Grade School, Nottingham. B.Sc. (Hons. Vict.) in Chemistry. Was for four years a Student in the Honours School of Chemistry at the Owens College, Manchester.

H. B. Dixon. G. H. Bailey.
W. H. Perkin, jun. A. William Gilbody.
W. T. Lawrence. William A. Bone.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

Issued 26/4/1899

PROCEEDINGS
OF THE
CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 15. No. 208.

April 20th, 1899. Professor Thorpe, F.R.S., President, in the Chair.

Messrs. A. J. While, W. J. Sell, and S. Godfrey Hall were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Robert Henry Aders, 28, St. John's Wood Road, N.W.; Percy Bean, 42, Granville Road, Blackburn; Walter Lionel Blackman, Mostyn, Mount Nod Road, Streatham, S.W.; Wilfred Carpmael, 24, Southampton Buildings, Chancery Lane, W.C.; Frederick Doyle, 8 Woodlands Terrace, Middlesbrough; Frederick Charles Dunscombe, 54, Woodstock Road, Bristol; William Frederick Eichenauer, 58A, Maryon Road, Old Charlton, Kent; Friedrich Noel Ashcroft Fleischmann, Magdalen College, Oxford; Frederick Hutton Getman, 196, Atlantic Street, Stamford, Conn., U.S.A.; Julius Hübner, 24, Delanney's Road, Crumpsall, Manchester; Edward Charles Johnson, Lithgow, N.S.W., Australia; Arthur Alexander Leon, 13, Cleveland Square, Hyde Park, W.; James McAlley, Bankside, Falkirk; George Alfred Parkes, Muckomore Bleach Works, co. Antrim, Ireland; Stanley John Peachey, 48, Grange Road, S.E.; Sidney Rossiter, 19, Ranelagh Road, West Green, N.; William Frederick John Shepheard, 12, Bridge Street Row, Chester; John Ward Stainer, 103, Cheriton Road, Folkestone; George Hardstaff West, Frankwell, Llanidloes.

The following Certificate was authorised by the Council under Bye-law I (3).

Bennetts, Benjamin Harvey,
Gormanston, Mt. Lyell, Tasmania.
Assayer. Two years Student at the School of Mines, Ballarat

Victoria. At present Assayer for the Mount Lyell Mining and Railway Company, Tasmania.

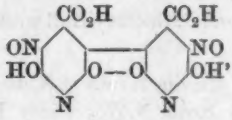
Albert H. Turton. Harold Harris.

John Provis.

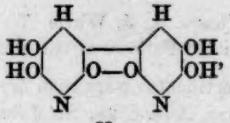
Of the following papers, those marked * were read :—

*48. "The synthesis of some $\beta\beta'$-dipyridyl derivatives from citrazinic acid." By W. J. Sell, M.A., and H. Jackson, B.A., B.Sc.

The present communication deals mainly with the constitution of some of the compounds described by Sell and Easterfield (*Trans.*, 1893, 63, 1035), of which little more than an analysis and brief description were given. It is now shown that citrazinic acid yields a nitroso-derivative, to which the formula $CO_2HC\langle\begin{matrix}CH_2 & CO\\ CNO\text{–}C(OH) & N\end{matrix}\rangle$ may be assigned. This compound is readily oxidised by nitrous or nitric acids, producing the yellow acid represented by formula I,



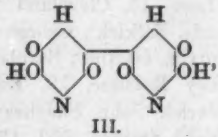
I.



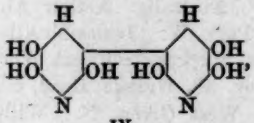
II.

both these substances, on reduction, readily yield a very sparingly soluble compound having a bronze-like appearance, and possessing the constitution represented by formula II.

The bronze-like substance reacts readily when boiled with fuming hydriodic acid and phosphorus, producing $\alpha\alpha'$-diglutaric acid, thus showing that these substances are derivatives of dipyridyl. With nitric acid, it produces a golden-yellow, crystalline compound, to which the authors assign the constitution represented by formula III,



III.



IV.

This substance is readily reduced to the bronze-like compound, and further reduction, either by hydriodic acid or stannous chloride, produces the hexhydroxy-derivative having the constitution represented by formula IV.

If the bronze-like substance be heated at 100° with chlorosulphonic acid, a white, crystalline compound, having the formula $C_{10}H_4Cl_2O_3$, is produced.

***49. "Action of hydrogen peroxide on carbohydrates in the presence of iron." By R. S. Morrell, M.A., Ph.D., and J. M. Crofts, B.A., B.Sc.**

Cross and Bevan, in their paper on the reaction of carbohydrates with hydrogen peroxide (*Trans.*, 1898, 73, 463), showed that substances which reacted with phenylhydrazine in the cold were formed. In September, 1898, some results of the reaction were communicated to the British Association, in which it was shown that the first product was undoubtedly glucoson. The glucoson had not then been isolated, but was identified by means of the osazone formed by the action of phenylhydrazine *in the cold*, and by the isolation of the methyl phenyl glucosazone, precipitated also in the cold. The formation of this methyl phenyl glucosazone was considered by Fischer to be one of the characteristic tests for the presence of glucoson.

The action of hydrogen peroxide in the presence of ferrous salts has been extended to levulose and galactose, to the pentose arabinose, and to the methyl pentose, rhamnose. Of these, levulose and arabinose have yielded results which are similar to those obtained with glucose, namely, the formation of an oson.

The oson was detected, in the case of glucose, by the formation, in each instance in the cold, of phenyl glucosazone (m. p. 205°), and of methyl phenyl glucosazone (m. p. 152°), both the glucosazones being analysed. The solution of the glucoson reduces Fehling's solution in the cold, and more strongly so on slightly warming. It yields precipitates in the cold with diamines, with hydrazine, and with substituted hydrazines.

It might be that the osazones were formed from the glucose directly, and not from the oson; the solution, however, after fermentation at 30°, was still found to react quite as readily with hydrazines in the cold. A small quantity of the oson isolated was found to have properties like those ascribed by Fischer to glucoson.

The behaviour of levulose is almost identical with that of glucose under like conditions of treatment. The oson formed is glucoson, and its identification rests on the same evidence as that given for glucoson from glucose.

With regard to arabinose, the action is again similar to that which takes place in the case of the hexoses. Arabinoson is undoubtedly formed, and its identification is established by the formation of arabinosazone in the cold, and more completely by the formation of methyl phenyl arabinosazone in the cold, whereas arabinose and methyl phenyl hydrazine, even with excess of the hydrazine and after warming on the water-bath, were found to form methyl phenyl arabinose hydrazone.

Galactose and rhamnose, under like conditions of treatment, also form substances of the nature of an oson, which are being investigated.

The action of bromine at 40° on the solution of the glucoson gives a liquid still strongly reducing, which reacts easily with phenylhydrazine, and forms, in the case of levulose, a soluble calcium salt of a dibasic acid, which is probably an oxysaccharic acid.

The course of the reactions may, perhaps, be expressed by the following equations.

$$\underset{\text{Glucose.}}{CHO\cdot CHOH\cdot(CHOH)_3\cdot CH_2OH} + O = \underset{\text{Glucoson.}}{CHO\cdot CO\cdot(CHOH)_3\cdot CH_2OH} + H_2O.$$

$$\underset{\text{Levulose.}}{CH_2OH\cdot CO\cdot(CHOH)_3\cdot CH_2OH} + O = \underset{\text{Glucoson.}}{CHO\cdot CO\cdot(CHOH)_3\cdot CH_2OH} + H_2O.$$

$$\underset{\text{Arabinose.}}{CHO\cdot CHOH\cdot(CHOH)_2\cdot CH_2OH} + O = \underset{\text{Arabinoson.}}{CHO\cdot CO\cdot(CHOH)_2\cdot CH_2OH} + H_2O.$$

DISCUSSION.

Mr. FENTON said that he was very glad that Dr. Morrell had succeeded in bringing his observations on carbohydrates to the present stage. His results now nearly completed the series of investigations which had been undertaken with a view of studying the behaviour of typical hydroxy-compounds towards oxidising agents in presence of iron.

***50. "The condensation of oxalic acid and resorcinol." By John Theodore Hewitt and Arthur Ernest Pitt.**

The condensation of oxalic acid and resorcinol, on heating with concentrated sulphuric acid, has been studied by von Baeyer (*Ber.*, 1871, 4, 662) and Gukassianz (*Ber.*, 1878, 11, 1184). The former stated that the product obtained closely resembled euxanthone, the latter that two isomeric substances were formed, both having the formula $C_{14}H_8O_5$, but whilst one was soluble in alcohol and gave non-fluorescent alkaline solutions, the other was insoluble in alcohol, but dissolved with a fine, moss-green fluorescence.

The authors have studied the former of these two products, which is the chief product of the reaction. It is distinct from the substances obtained by Claus and Andreae (*Ber.*, 1877, 10, 1305; 1881, 14, 2563) and von Georgievics (*Mitt. technol. Gewerb-Mus. Wien*, 1898, [ii], 8, 364). These chemists used an excess of oxalic acid as a condensing agent, and employed a higher temperature. Gukassianz misinterpreted the results obtained on combustion; his compound really has the formula $C_{20}H_{14}O_7$, and is probably a carboxylic acid. In addition to further analyses of this compound, the authors describe the following derivatives.

Sodium and lead salts, $C_{20}H_{13}O_7Na$, $(C_{20}H_{13}O_7)_2Pb$. Triacetylated lactone, $C_{20}H_9O_6(C_2H_3O)_3$. Triacetylated acid, $C_{20}H_{11}O_7(C_2H_3O)_3$.

Tetracetylated lactone of leuko-acid, $C_{20}H_{10}O_6(C_2H_3O)_4$. Product obtained from acid and benzoyl chloride, (?) $C_{14}H_7O_5(C_6H_5CO)$. Dinitro-lactone, $C_{20}H_{10}(NO_2)_2O_6$. Sodium salt of dinitro-acid, $C_{20}H_{11}(NO_2)_2O_7Na$. Triacetylated dinitro-lactone, $C_{20}H_7(NO_2)_2O_6(C_2H_3O)_3$. Tetrabrominated acid, $C_{20}H_{10}Br_4O_7$.

From the composition of the compounds described, the authors consider that the acid must be represented by the formula $[C_{18}H_9(:O)(OH)_4]:C\cdot CO_2H$.

51. "Ethyl ammonium sulphite." By Edward Divers and Masataka Ogawa.

Dissolved in alcohol, sulphur dioxide and ammonia combine with each other and the alcohol to form a new salt, ethyl ammonium-sulphite, which is a crystalline solid, subliming undecomposed in dry air, soluble in alcohol, insoluble in ether, and at once changed by water into alcohol and ammonium pyrosulphite. Hence, in preparing the salt, the absence of water must be carefully secured. Ethyl ammoniumsulphite belongs to the series of new sulphites, or metal-sulphonates discovered within the last few years:—Phenyl sodium-sulphite (Schall, 1892); methyl magnesiumsulphite (Szarvasy, 1897); methyl and ethyl sodiumsulphites and ethyl potassiumsulphite (Rosenheim and Liebknecht, 1898), which are distinguished from alkylsulphonates in at once decomposing with water into phenol or alcohol and pyrosulphite, and in being formed by the union of sulphur dioxide with metal alkoxide or ammonium alkoxide. Warlitz's potassium ethyl sulphite has been shown by Rosenheim and Liebknecht to be only potassium ethylsulphonate. The new salts are not decomposed by excess of sulphur dioxide; Rosenheim and Liebknecht, who found that they were, must have allowed moisture to enter their vessels.

52. "Ethyl ammonium selenite and non-existence of amidoselenites (selenosamates)." By Edward Divers and Seihachi Hada.

Selenium dioxide and ammonia, dissolved together in well-cooled alcohol, in the absence of any water, form a new salt, ethyl ammonium selenite, soluble in alcohol, insoluble in ether, and at once decomposed by water into acid ammonium selenite and alcohol. The salt soon begins to decompose at the common temperature, selenium being one of the products. Hinsberg obtained, in 1890, what appears to have been ethyl hydrogen selenite and ethyl phenylammonium selenite.

When water is also present, the ammonia and selenium dioxide do not unite with the alcohol, but with the water to form the ammonium

selenites, a fact known to Berzelius. Cameron and Macallan (1888), proceeding apparently in the way the authors have prepared ethyl ammonium selenite, obtained instead salts which they describe as being selenosamates. But Cameron and Macallan record no property of their selenosamates which can serve to distinguish them from the half-acid and three-fourths-acid ammonium selenites, except their chemical composition, which was determined by methods of doubtful accuracy. The authors, therefore, believe that Cameron and Macallan cannot have taken sufficient precautions to exclude all moisture in their experiments, and conclude that there is no reliable evidence for the existence of amidoselenites. Accordingly, selenious acid seems to form no compounds analogous to amido-, imido-, or nitrilo-sulphates, any more than it forms salts like alkylsulphonates or salts having the constitution of metal sulphites.

Incidentally, the authors obtained, in the pure state, normal ammonium selenite, half-acid ammonium selenite, and three-fourths-acid ammonium selenite.

53. "The allotropic modifications of phosphorus." By D. L. Chapman, B.A.

From experiments performed by the author, the following conclusions have been drawn.

(1.) "Metallic" and red phosphorus are identical. This is proved by their similarity in appearance when viewed under the microscope. The alleged higher vapour tension of some varieties of red phosphorus is due to impurity, which on heating decomposes with formation of phosphorus vapour.

(2.) The vapours of red and ordinary phosphorus are identical. The vapour density of ordinary phosphorus has been determined at the boiling points of mercury and of sulphur, and agrees closely with the density calculated on the assumption that the molecule consists of four atoms, although the results obtained by Mitscherlich and by Deville and Troost at higher temperatures would scarcely lead one to suspect that this would be the case.

(3.) Red phosphorus melts, forming ordinary phosphorus, under pressure at the melting point of potassium iodide. This point on the pressure temperature diagram the author proposes to call the triple point of red phosphorus. Melted ordinary phosphorus thus becomes superfused red phosphorus, and superfused ordinary phosphorus becomes the superfused liquid of both varieties. At ordinary temperatures, red phosphorus is stable and white phosphorus unstable. Phosphorus, therefore, appears to possess in a remarkable degree the property of remaining in an unstable condition.

54. "On the interaction of mercurous and mercuric nitrites with the nitrites of silver and sodium." By P. C. Rây, D.Sc.

(1.) *Mercuric and sodium nitrites.* To the neutral solution of mercurous and mercuric nitrites, the products of the dissociation of mercurous nitrite (*Trans*, 1897, 71, 340), sodium chloride is added to remove mercurous salts. The filtrate containing mercuric and sodium nitrites, and possibly a small quantity of sodium chloride, is allowed to evaporate spontaneously. In course of time, an orange-red, crystalline deposit is formed, followed by iodine-like scales, and finally crystals of sodium nitrate. Sometimes sodium nitrate is the only substance obtained. Unless sodium chloride is present, the coloured compounds are not formed. Analysis seems to show that the formula of the coloured substances is $HgCl_2,2HgO,\frac{1}{2}H_2O$, but they lose no weight in a desiccator over sulphuric acid nor when kept at 100°, but if heated in a bulb tube a deposit of moisture is invariably noticed. Millon, Thummel, Volhard, and Haack have described very similar compounds with the formula $HgCl_2,2HgO$, but no mention is made of any hydrated modification.

(2.) *Mercurous and silver nitrites.* To a hot solution of mercurous nitrite (containing mercuric nitrite) solution of silver nitrite was added. There was no effervescence, but the liquid at once became cloudy, and was allowed to stand overnight. Next day a clear solution was obtained, having at the bottom a layer of dirty grey mercury, and above it a deposit of shining, minute crystals of silver.

Careful analyses showed that, not only was there no loss of nitrogen during the reaction, but that it remained entirely in the form of nitrite.

With dilute solutions no silver was precipitated. In the reaction between mercurous and sodium nitrites, the nitrogen remained as nitrite, the mercurous nitrite decomposing entirely into mercuric nitrite and mercury.

The true explanation of the reactions has yet to be found, and with this end in view the author intends to make further experiments with solutions of the nitrites in varying degrees of dilution.

55. "β-Isopropylglutaric acid." By F. H. Howles and Jocelyn F. Thorpe.

β-Isopropylglutaric acid was originally prepared by Schryver, by the reduction of terpenylic acid and synthesised by him in small quantities by the action of ethylic sodiomalonate on ethylic isobutylenemalonate (*Trans.*, 1893, 1345); later, Knoevenagel (*Ber.*, 1898, 31, 2585) pre-

pared it by the condensation of isobutaldehyde with ethylic malonate; Schryver's acid melted at 99—100°, Knoevenagel's at 96·5—97°. The authors find that by far the largest yield of this acid is obtained in the following way.

Ethylic β-isopropylacrylate. $Pr^{\beta}\cdot CH{:}CH\cdot CO_2Et$, prepared by eliminating hydrogen bromide from ethylic α-bromisobutylacetate by means of diethylaniline, is a mobile liquid, boiling at 174°, which, on condensation with ethylic sodiocyanacetate in alcoholic solution gives a mixture of a neutral and a hydrogen ethylic salt. Ethylic α-cyano-β-isopropylglutarate, $EtO_2C\cdot C(CN)H\cdot CH(Pr^{\beta})\cdot CH_2\cdot CO_2Et$, is a colourless oil boiling at 195° (30 mm.), whilst the hydrogen ethylic salt, $HO_2C\cdot C(CN)H\cdot CH(Pr^{\beta})\cdot CH_2\cdot CO_2Et$, is a dark coloured oil which splits off carbon dioxide on distillation and passes into ethylic γ-cyano-β-isopropylbutyrate, $CN\cdot CH_2\cdot CH(Pr^{\beta})\cdot CH_2\cdot CO_2Et$, a mobile liquid boiling at 234°.

The neutral ethylic salt on hydrolysis with methyl alcoholic potash, yields a solid potassium salt, which, on boiling a short time with concentrated hydrochloric acid, becomes the imide, $(Pr^{\beta})CH\langle\begin{matrix}CH_2CO\\CH_2CO\end{matrix}\rangle NH$, a solid substance crystallising from water in lustrous plates melting at 120°, and which is quantitatively converted into β-isopropylglutaric acid on boiling for two hours with a 50 per cent. solution of sulphuric acid.

β-Isopropylglutaric acid, $HO_2C\cdot CH_2\cdot CH(Pr^{\beta})\cdot CH_2\cdot CO_2H$, prepared either in this way or by the direct hydrolysis of the hydrogen ethylic salt with sulphuric acid, crystallises from water in needles melting at 100°, and on treatment with acetyl chloride yields a liquid anhydride boiling at 171° (30 mm.), and an anilic acid crystallising from dilute alcohol in plates melting at 121°.

This acid does not appear to be identical with that obtained by Angeli and Rimini (*Gazz. Chim.*, 26, 36) from isocamphor on oxidation with potassium permanganate, which melts at 96° and gives an anhydride melting at 60°, further the dissociation constant K 0·0646 of the authors' acid, as found by Mr. Lidbury, does not agree with K 0·0052 of Angeli and Rimini's acid.

56. "The synthesis and preparation of terebic and terpenylic acids." By W. Trevor Lawrence.

The tertiary hydrogen atom in monobasic aliphatic acids is readily oxidised by potassium permanganate (R. Meyer and Fittig).

The author has applied this method to the synthesis of terebic and terpenylic acids.

β-Isopropylglutaric acid is readily oxidised by chromic acid mixture,

with the formation of terpenylic acid, confirming Wallach's formula for this acid, namely, $\begin{matrix} Me_2—C—O— \\ | \quad\quad\quad | \\ CO_2H\cdot CH_2\cdot CH\cdot CH_2CO \end{matrix}$. The synthetic acid is identical with the acid obtained by oxidation of oil of turpentine, melting when anhydrous at 89°, and with 1 mol. H_2O at 56°. It is oxidised by permanganate with formation of terebic acid, and gives the characteristic silver salt, $C_8H_{11}O_4Ag$.

Isopropylsuccinic acid is also easily oxidised by chromic acid mixture to terebic acid, $C_7H_{10}O_4$, which is identical in all respects with the acid obtained by the oxidation of oil of turpentine.

The synthetic acid melts at 175°, and gives the characteristic barium salt of diaterebic acid, $C_7H_{10}O_5Ba,3H_2O$. Under similar conditions, $\beta\beta$-dimethylglutaric acid remains unchanged.

The yield of the lactone acid is 50—60 per cent., the rest being unchanged acid.

Further, it is shown that the separation of terebic and terpenylic acids is easily and completely effected by spreading the mixture of acids on porous plates and heating at 90°; the terebic acid remains as a dry powder on the surface of the plate, and the terpenylic acid is obtained by extracting the plate with water. The author is further engaged in investigating the oxidation products of other similarly constituted acids, and also the action of hydrobromic acid on terebic and terpenylic acids.

57. "Position-isomerism and optical activity: the comparative rotatory powers of methylic and ethylic ditoluylglycerates." By Percy Frankland, F.R.S., and Henry Aston.

This forms a continuation of the work on the same subject by P. Frankland, McCrae, and Wharton (Trans., 1896, **69**, 1309, 1583; 1898, **73**, 307; 1899, **75**, 337), the authors having prepared and examined the methylic and ethylic salts of the three isomeric ditoluylglyceric acids. Methylic di-*p*-toluylglycerate (inactive) melts at 98°, the corresponding active salt at 102°; ethylic di-*p*-toluylglycerate melts at 69°; all the other compounds are liquids. The following are the specific rotations:—

Methylic di-*p*-toluylglycerate.....	$[\alpha]_D^{20°} = +41{\cdot}21°$
Ethylic ,, ...	,, $= +42{\cdot}41$
Methylic di-*m*-toluylglycerate	,, $= +26{\cdot}40$
Ethylic ,, ...	,, $= +26{\cdot}89$
Methylic di-*o*-toluylglycerate.....	,, $= +20{\cdot}19$
Ethylic ,, ...	,, $= +21{\cdot}64$

The corresponding dibenzoylglycerates, previously prepared by P. Frankland and MacGregor (Trans., 1896, 69, 104) have the following rotations :—

Methylic dibenzoylglycerate	(m. p. 58·9°) ...	$[\alpha]_D^{20°} = +26·67°$
Ethylic „	(m. p. 25°) ...	„ $= +26·08$

Thus in this series, again, the *p*-toluyl group has the greatest, and the *o*-toluyl group the least, rotatory effect. The rotatory effect of the benzoyl is almost identical with that of the *m*-toluyl group.

The dextrorotation of all these compounds diminishes with increase of temperature.

The rotatory effects of the isomeric toluyl groups is again found to follow in the same order as that of their molecular volumes, the *p*-toluyl having the largest, and the *o*-toluyl-compounds the smallest, molecular volumes. The molecular volumes of all these compounds are distinctly in excess of the values calculated by means of Traube's formula, and thus afford no evidence of association.

58. "Fencholenic acid." By G. B. Cockburn, B.A., B.Sc.

The author shows that fenchonoxime, by treatment with dilute sulphuric acid, gives, not one nitrile, as Wallach states (*Annalen*, 1891, 263, 136), but a mixture of two isomerides. Of these, one (β) passes easily on saponification to a solid unsaturated acid, $C_9H_{15}CO_2H$, m. p. 72—73°, b. p. 259—260°. The other (α) is very stable, and only gives an acid after long saponification. This acid is isomeric with the former, but is liquid, and boils at 254—256°. Wallach describes the acid he obtained as a liquid, but it is probably a mixture of the above α- and β-acids. The boiling point of the nitrile, as given by Wallach, is 217—218°, whilst that of the pure β-nitrile reformed from the pure acid is 211—212°, and of the α-, 217—219°. Owing to the difference in behaviour of these two nitriles towards alcoholic potash, the separation of the two acids is comparatively simple.

This behaviour of fenchonoxime bears out the analogy existing between camphor and fenchone. The oximes of both these bodies, by the action of dilute acid, lose a molecule of water in two different ways, and give two isomeric unsaturated nitriles in each case; and these in their turn yield two corresponding acids, one solid, the other liquid.

59. **"The action of certain acidic oxides upon salts of hydroxy-acids. Part IV." By G. G. Henderson, D.Sc., M.A.; T. W. Orr, and R. J. G. Whitehead.**

The paper contains the results of investigations carried on in continuation of those formerly communicated to the Society (*Trans.*, 1895, 67, 102 and 1030; 1896, 69, 1451), and a discussion of the constitution of the compounds of the tartar emetic type.

Sodium, *potassium*, and *ammonium molybdicitrates* were prepared by boiling molybdenum trioxide with aqueous solutions of the corresponding primary citrates. They have the formula $MoO_2(C_6H_6O_7M')_2,xH_2O$, crystallise in colourless prisms, are readily soluble in water, and are decomposed by heat or light. The barium salt, $MoO_2(C_6H_6O_7)_2Ba,5H_2O$, obtained by precipitation, is a white, crystalline powder almost insoluble in water. Decomposed by dilute sulphuric acid, it yields a solution which appears to contain molybdicitric acid, $MoO_2(C_6H_7O_7)_2$.

Tungstic oxide, boiled with solutions of mono-alkali citrates, gave *double tungsticitrates* of the formula $WO_2(C_6H_6O_7M')_2,C_6H_7O_7M',xH_2O$; the simple salts are not obtained. These salts form small, colourless crystals very readily soluble in water, and are not decomposed when heated to 120°. The double barium salt, $2WO_2(C_6H_6O_7)_2Ba$, $(C_6H_7O_7)_2Ba,10H_2O$, prepared by double decomposition, crystallises in minute needles, soluble in water.

Sodium, *potassium*, and *ammonium molybdimalates*, $MoO_2(C_4H_4O_5M')_2,xH_2O$, were prepared like the molybdicitrates. The potassium salt crystallises in large, the sodium salt in small, colourless prisms, and the ammonium salt is a white, crystalline powder. All are readily soluble in water, and easily decomposed by exposure to heat or light. Another molybdimalate of sodium, of the formula $MoO_2{:}C_4H_3O_5Na,1\frac{1}{2}H_2O$, was prepared by heating a solution of monosodium malate with excess of molybdic oxide. It crystallises in long, colourless needles, which are soluble in water, is very sensitive to light, and is decomposed by heating to about 90°.

Tungstic oxide is only dissolved with difficulty by solutions of alkali malates, but some *tungstimalates*, $WO_2(C_4H_4O_5M')_2,xH_2O$, were prepared. The sodium salt crystallises in small, the potassium salt in long, needles, the ammonium salt in delicate leaflets. They are readily soluble in water, and can be heated to 105° without decomposition.

With solutions of mono-alkali mucates, molybdic oxide gives in the first instance unstable double salts, $2(MoO_2{\cdot}C_6H_7O_8M')$, $C_6H_9O_8M',xH_2O$, which are easily soluble in water, and yield the simple *molybdimucates*, $MoO_2{:}C_6H_7O_8M',xH_2O$. The potassium and ammonium salts are white,

crystalline powders, fairly easily soluble in water, and decomposed by heating to about 90°. When dry they are fairly stable to light, but their solutions are quickly acted upon.

Potassium tungstimucate, $WO_2{:}C_6H_7O_8K,3H_2O$, was prepared similarly, but with difficulty. It forms minute, lustrous crystals, and is extremely readily soluble in water, and more stable towards heat or light than the molybdimucate.

Potassium molybdilactate, $MoO_2(C_3H_4O_3K)_2$, the only crystalline derivative of lactic acid we have succeeded in preparing, was obtained in the form of small, colourless crystals, very readily soluble both in water and in dilute alcohol. It is not very sensitive to light when dry.

Silica was found to be almost insoluble, even when used in the hydrated state, in solutions of all the salts examined.

Sodium, potassium, ammonium titanitartrates, $TiO(C_4H_4O_6M')_2,xH_2O$, were prepared in the usual way. Hydrated titanic oxide was used, because the anhydrous oxide is practically insoluble in solutions of tartrates. The salts crystallise in small, colourless prisms readily soluble in water. Alcohol precipitates from a solution of the ammonium salt a crystalline solid whose composition approximates to the formula $TiO{:}C_4H_3O_6NH_4$. A white barium salt, almost insoluble in water, is obtained by precipitation.

The corresponding *stannitartrates*, $SnO(C_4H_4O_6M')_2,xH_2O$, were prepared similarly. They form small, colourless crystals fairly easily soluble in water. Heating of their solutions in water for any length of time causes slow decomposition of the salts, but in the dry state they are quite stable. From solutions of the potassium and ammonium salts, alcohol precipitates crystalline solids, which appear to have the formula $SnO{:}C_4H_3O_6M'$. A white barium salt, almost insoluble in water, was also prepared.

Potassium titanicitrate, $TiO(C_6H_6O_7K_2),H_2O$, and *ammonium stannicitrate*, $SnO(C_6H_6O_7NH_4)_2,\frac{1}{2}H_2O$, were obtained by a similar process, though with some trouble. They form small, white crystals very readily soluble in water and soluble in dilute alcohol. They are stable when dry, but gradually decompose if their aqueous solutions are heated.

The hydrated dioxides of titanium and tin were found to dissolve in boiling aqueous solutions of mono-alkali malates, but no definite compounds were isolated.

With some difficulty, a *potassium titanimucate*, $TiO{:}C_6H_7O_8K,3H_2O$, was prepared in the form of small, white crystals, easily soluble in water, not sensitive to light, and not decomposed at 100°. No corresponding compound of tin could be obtained.

ADDITIONS TO THE LIBRARY.

Donations.

Berthelot, M. Chaleur Animale. Principes chimiques de la Production de la Chaleur chez les êtres vivants. I. Notions Générales. Pp. xvi + 169. II. Données Numériques. Pp. 148. Paris, 1899. From the Author.

Bolton, H. C. A Select Bibliography of Chemistry, 1492—1897. First Supplement. Pp. ix + 489. Washington, 1899. Smithsonian Miscellaneous Collections, 1170. From the Smithsonian Institution.

Mason, W. P. Examination of Water (Chemical and Bacteriological). Pp. 135. New York, 1899. From the Publishers.

Reychler, A. Outlines of Physical Chemistry. Translated by John McCrae. Pp. xvi + 276. London, 1899. From the Publishers.

II. *Purchase.*

Boltzmann, Ludwig. Vorlesungen über Gastheorie. II. Theil. Theorie van der Waals'; Gase mit zusammergesetzten Molekülen; Gasdissociation; Schlussbemerkungen. Pp. x + 265. 8vo. Leipzig 1898.

Van der Waals, J. D. Die Continuität des gasförmigen und flüssigen Zustandes. Zweite, verbesserte Auflage. I. Theil. Pp. vii + 182. 8vo. Leipzig 1899.

Pamphlets.

Australasian Association for the Advancement of Science. Report on the Composition and Properties of the Mineral Waters of Australasia. Sydney 1898.

Spring, W. Sur l'origine de la couleur bleue du ciel. Bruxelles 1898.

True, F. W. An Account of the United States National Museum. From the Report of the U.S. National Museum for 1896. Washington 1898.

COLLECTIVE INDEX.

Fellows can obtain the Collective Index 1873—1882 from the Assistant Secretary at the price of 10*s*., or 11*s*. including carriage. The price of the Collective Index 1883—1892 is 16*s*. including carriage.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in June. Forms of application for Grants can now be obtained from the Assistant Secretary.

At the next meeting, on May 4th, there will be a ballot for the election of Fellows, and the following papers will be communicated by the authors:—

"On the combustion of carbon disulphide." By Harold B. Dixon and E. J. Russell.

"The action of nitric oxide on nitrogen peroxide." By Harold B. Dixon and J. D. Peterkin.

"On the mode of burning of carbon." By Harold B. Dixon.

"Crystalline glycollic aldehyde." By H. J. H. Fenton and Henry Jackson.

"On the blue salt of Fehling's solution and other cupro-tartrates." By Orme Masson and B. D. Steele.

"The preparation of acid phenolic salts of dibasic acids." By S. B. Schryver, D.Sc., Ph.D.

"The maximum pressure of naphthalene vapour." By R. W. Allen, M.A.

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PROCEEDINGS
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May 4th, 1899. Professor Thorpe, F.R.S., President, in the Chair.

Messrs. David Hooper and W. H. Mills were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Henry Meldola Danziger, Clent House, Woodland Road, Northfield, Birmingham; William Gordon Fraser, Golspie, St. Albans; Henry Royal-Dawson, 3, Kenilworth Road, Ealing, London, W.; Samuel Stansfield, White Lee, Mytholmroyd, Manchester; Christopher Joseph Whittaker, Willow House, Blackburn Road, Accrington.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—

James Herbert Allworthy, Peter Auchinachie, Clement Harrison Baker, Frederick James Beale, Frank Belton, Benjamin Harvey Bennetts, Alfred Ernest Bond, George Smith Bratby, Kendall Colin Browning, B.A., William Collingridge, M.A., Robert D. Connell, Charles Robert Darling, Harold Francis Carl Goltz, Percy Haigh, John Elias Hughes, Archibald Glen Kidston Hunter, Lauder William Jones, B.A., Ph.D., Thomas Judge, B.A, Robert William Lindsey, James MacLeod, William McConnell, Wilfred Walter Morris, Laurence C. Panting, B.A., M.B., Frederick Williams Pittuck, Harold McLean Read, S. B. Schryver, D.Sc., Ph.D., Maurice Emile Schweich, Edward Thomas Shelbourn, Arthur John Shelton, Harry Alexander Thiersch, Robert Tatlock Thomson, Richard Threlfall, Ernest Albert Tyler, B.A., Arthur Luvian Wade, Allan Frederick Walden, M.A., Charles Walker, Fred Sheasby Watson, B.Sc.

Of the following papers, those marked * were read :—

***60. "On the combustion of carbon disulphide." By Harold B. Dixon and E. J. Russell.**

The authors have investigated the temperature of ignition of carbon disulphide in air, its stability on heating, its mode of burning in air in the divided flame, and its explosion with oxygen.

Experiments on the ignition point of carbon disulphide showed considerable variations. It was found that the vapour undergoes a phosphorescent combustion in air similar to that of phosphorus, sulphur, ether, &c. This phosphorescence is well seen in a dark room when the vapour impinges on a glass vessel at 230°. The lowest temperature at which actual ignition was observed was 232°. Carbon disulphide distilled in a current of nitrogen through a porcelain tube heated to 400° showed no visible decomposition. When carbon disulphide was sealed up in a glass tube and submitted to prolonged heating at 230°, a slight yellow film formed on the glass. A similar film was produced by the prolonged action of bright light.

Although carbon disulphide is decomposed by a violent shock (*e.g.*, an explosion of fulminate) into its elements, this decomposition is not propagated through its vapour as an explosion, but dies out. When carbon disulphide is exploded with defect of oxygen, it does not yield a deposit of carbon. When it is exploded in a long tube with an excess of oxygen, the products of the combustion are mainly those required by the equation $CS_2 + 3O_2 = CO_2 + 2SO_2$, but there are always present small quantities of carbon disulphide, oxysulphide, and monoxide with the excess of oxygen.

When carbon disulphide is exploded in a long tube with insufficient oxygen for complete combustion, the products are carbon dioxide and sulphur dioxide along with carbon oxysulphide and monoxide, sulphur, and unchanged carbon disulphide. As the oxygen is gradually diminished, the amount of sulphur dioxide falls off, whilst the carbon monoxide increases. The authors were unable to set up the explosion-wave in mixtures containing less than 40 per cent. of oxygen. So far as the experiments could be carried, there was always a division of the oxygen between the carbon and sulphur. No simple equation expresses the mode of burning. In the incomplete combustion of carbon disulphide, the sulphur was deposited partly in the 'liquid' condition.

The maximum velocity of the explosion-wave was found when the oxygen just sufficed for complete combustion.

When carbon disulphide vapour and air are burnt as the Smithells' divided flame, the products of the inner flame are sulphur dioxide and carbon monoxide in nearly equal volumes, some unchanged carbon

disulphide, and only small quantities of carbon dioxide and oxysulphide.

Discussion.

Professor Tilden said that it seemed to him impossible to determine or to state exactly the temperature of ignition of any combustible substance, inasmuch as this depends largely upon conditions such as the proportion of air present, and especially the extent of the heated surface by which the action is started. As an example, the very small, though very hot, sparks from a flint and steel are known to be incapable of inflaming a mixture of coal gas and air, while a red-hot iron bar, though at much lower temperature, does cause ignition by reason of its greater mass.

Dr. Wynne said that in purifying carbon bisulphide for the purpose of determining its magnetic rotation, the late Mr. Rodger, by exposing the liquid to sunlight, had obtained some quantity of the brown substance with a view of determining its composition. The prevalent idea seemed to be that the brown substance was a subsulphide, possibly C_2S_3, and it would be interesting to know whether Professor Dixon had any evidence bearing on the point.

Professor Smithells said that he could confirm Professor Dixon's remark as to the phosphorescent combustion of carbon disulphide. This substance might be added to the long list of carbon compounds which were capable of phosphorescent combustion. The combustion of carbon disulphide was of special interest from the fact that the flame did not exhibit the so-called carbon or candle spectrum, but this he believed could be explained by the masking effect of the burning sulphur. He had found that a burning mixture of ethylene and hydrogen sulphide gave no carbon spectrum, although an ethylene air flame of itself would of course do so. He had made some examination of the partial products of combustion of carbon disulphide; they were difficult to deal with, and he was glad that Professor Dixon had brought the inquiry to a successful issue. It was interesting to remark that some years ago Julius, from an examination of the spectrum of burning carbon disulphide, had concluded that some third substance besides carbon dioxide and water was formed, and he had detected carbon oxysulphide. Professor Dixon, however, had gone much further in establishing this fact.

***61. "The action of nitric oxide on nitrogen peroxide." By Harold B. Dixon and J. D. Peterkin.**

Some few years ago, the question was keenly debated whether nitrogen trioxide existed in the gaseous state. On both sides, the final appeal was made to the behaviour of nitric oxide when mixed

with gaseous nitrogen peroxide. Ramsay and Cundall (*Trans.*, 1895, 67, 672) broke an inner tube, containing nitric oxide over mercury, by pressing it against an outer tube containing the peroxide over mercury. No contraction was observed. The experiment proved that no considerable quantity of trioxide could have been formed on mixing the gases. Lunge and Porschnew (*Zeit. anorg. Chem.*, 1894, 7, 209) broke a thin glass diaphragm between a vessel containing nitric oxide and a similar one containing the peroxide. The gases showed a very slight expansion on diffusing "instead of the large contraction expected." The natural conclusion of chemists has been that "gaseous N_2O_3 apparently does not exist."

But the dissociation which nitrogen peroxide undergoes on diminution of pressure would have caused an appreciable expansion in these experiments if the nitric oxide had merely played the part of an inert gas.

The authors confirm Lunge and Porschnew's conclusion that a very slight alteration of volume occurs on mixing nitric oxide with the peroxide at 27°, but they show that a considerable expansion occurs when the peroxide mixes with nitrogen and other inert gases, and that this observed expansion is in close agreement with that calculated from Willard Gibbs' formulæ for the dissociation of the peroxide. The authors infer from their experiments that at 27° nitric oxide and peroxide combine to a limited extent to form an unstable compound, which is largely dissociated at this temperature, and undergoes increasing dissociation as the temperature is raised. The reversibility of the equation $N_2O_3 = NO + NO_2$ affords an easy explanation of the behaviour of the mixed gases towards reagents.

Discussion.

Professor Ramsay congratulated Professor Dixon on having shown that in the gases evolved from nitrous anhydride, which consist chiefly of a mixture of nitric oxide and peroxide, a small amount of gaseous nitrous anhydride is to be detected. The power of this mixture of gases to react as N_2O_3 is thus explained. In 1885, he (Professor Ramsay) stated that, as the result of experiments showing that, in the main, the gases obtained from liquid anhydride consist of NO_2, N_2O_4, and NO, "it cannot be taken as conclusive that no nitrous anhydride is present in the gaseous state"; and Professor Dixon has found that a small proportion does so exist. The proof is valuable, inasmuch as it explains why the mixture of gases can act on sulphuric acid, be absorbed by soda, and act as a diazotising agent.

Professor Dewar said that, in his paper, "Studies on the Electric Arc" (*Proc. Roy. Soc.*, 1880, 30, 85), experiments are described

showing the amount and character of the oxides of nitrogen produced when an arc is maintained in a cool dry moving atmosphere. The quantity of oxides formed did not exceed 1 gram per hour. As the solution of the oxides in concentrated sulphuric acid gave the same percentage of nitrogen whether treated directly with mercury or after careful dilution with water and subsequent titration of the solution with permanganate, it was inferred that the main product was gaseous nitrous anhydride.

Experiments are also described in an address on "Phosphorescence and Ozone" (*Proc. Roy. Inst.*, 1888, 12, 557), which have an important bearing on this question. A current of attenuated air was maintained in a small vacuum tube of the ordinary form, and after the passage of the electric discharge was allowed to expand into a glass cylinder 3 feet long and 6 inches in diameter, maintained at a pressure not exceeding 6 or 8 mm. by means of a large air pump. The result was the production of extraordinary phosphorescent effects in the stream of air. This phosphorescence is associated with the production of ozone and oxides of nitrogen, as it does not take place in the absence of oxygen. Recently, the phosphorescent glow was allowed to pass through some liquid air in order to condense and solidify the oxides of nitrogen and dissolve the ozone out of the moving, luminous gas stream. The result was that the clear liquid air soon became turbid from the formation of a precipitated greenish-blue solid. On filtering this off, it gave all the reactions of nitrous acid, and no ozone was found in solution. The colour of the body at the low temperature shows it was not N_2O_4, which is colourless. It might be, however, a mixture of nitric oxide and nitrous anhydride. On the other hand, it is possible that NO_2, the dissociated molecule of N_2O_4, may exist in the solid state at the very low temperature and be coloured.

Mr. C. E. Groves said that, many years ago, in the course of experiments on the preparation of nitrosyl sulphate, he had found that the brown vapours given off when arsenious anhydride was heated at 70° with nitric acid of sp. gr. = 1·3 were almost entirely absorbed by concentrated sulphuric acid. Crystalline nitrosyl sulphate was formed, and but little, if any, nitric acid, although the latter should have been produced if nitric peroxide had been present. More recently, he had observed that these same vapours, when passed into a mixture of crushed ice and water, were absorbed, forming a solution of nitrous acid.

Professor Tilden said it was generally acknowledged that nitrogen trioxide existed only in the form of the blue liquid, which becomes almost completely dissociated by vaporisation. Professor Dixon seemed to have proved that in this case, as in so many others, a dis-

sociable compound is more stable in the presence of the products of its dissociation.

*62. "On the mode of burning of carbon." By Harold B. Dixon.

In the combustion of carbon, the formation of carbon dioxide is usually described as being due to a single and direct action between carbon and oxygen; it is stated or implied that carbon monoxide is only formed by a secondary action between carbon dioxide and carbon. The only experiments which claim to prove this are the two series made by Julius Lang (*Zeit. phys. Chem.*, 1888, **2**, 168).

The author repeated Lang's experiments, and found that when oxygen was passed over carbon heated to 500° (a temperature at which Lang showed carbon dioxide was not reduced by carbon), even in a very slow stream, some carbon monoxide was always formed.

Under conditions far less favourable for the reduction of carbon dioxide than in Lang's experiments, viz., by passing a mixture of carbon dioxide with 6—8 per cent. of oxygen over carbon heated to 500°, some carbon monoxide was always formed.

Lang's more important argument depends on his second series of experiments, which consisted in passing a mixture of oxygen, carbon monoxide, and nitrogen over carbon at 500°. He found that with a slow stream the carbon monoxide remained unchanged in amount, whilst all the oxygen was converted into carbon dioxide; with a quicker stream, the proportion of carbon monoxide increased considerably, but with a still quicker stream it was much reduced. The author has made many experiments to test these results. When a mixture containing about 80 per cent. of oxygen and 20 per cent. of carbon monoxide, was passed quickly over coke heated to 500°, the blue flame of burning carbon monoxide was observed, and the amount of that gas found in the products was small. On lowering the rate of the gas stream, the flame was not formed, but the carbon glowed and the amount of carbon monoxide in the products increased. This reached a maximum and then diminished as the rate of the stream was continually lowered. With a very slow stream, from 2—4 per cent. of carbon monoxide was found in the products. These results are quite opposed to the conclusions drawn by Lang, viz., that carbon monoxide is unaltered when, mixed with oxygen, it is passed very slowly over carbon at 500°. His argument that carbon dioxide must be first formed is therefore invalid.

The results of the new experiments might be explained on either hypothesis if it be assumed that the molecule of the monoxide, or of the dioxide, as the case may be, formed by the direct union of the

elements at 500°, retains sufficient heat (from its heat of formation) to react with oxygen or carbon respectively. The experiments of Baker (*Phil. Trans.*, 1888, 179 A, 571), make it very probable that the carbon burns first to carbon monoxide.

Discussion.

Professor Clowes said that Haldane (*Trans. Inst. Mining Engineers*, 16, 470), had shown that a small proportion of carbon monoxide accompanied carbon dioxide in the products of the spontaneous oxidation of coal at ordinary temperatures. The carbon monoxide was detected by the reaction with diluted blood, its proportion was estimated by this colorimetric method, and the result confirmed by the ordinary gasometric method.

*63. "Crystalline glycollic aldehyde." By Henry J. Horstman Fenton and Henry Jackson.

It has previously been shown by one of the authors (*Trans.*, 1895, 67, 774) that dihydroxymaleic acid, when heated with water, breaks up almost quantitatively into glycollic aldehyde and carbon dioxide, $C_4H_4O_6 = C_2H_4O_2 + 2CO_2$.

The resulting solution, after purification by treatment with calcium carbonate and extraction with alcohol, yields, on evaporation in a vacuum, a colourless, sweet syrup, which was shown to be the aldehyde in nearly a pure state. Traces of the solvent used for purification, however, are obstinately retained, and various attempts have been made to obtain the substance absolutely pure.

It was further shown (*Trans.*, 1897, 71, 375) that this syrup, when heated to 100° in a vacuum, polymerises to a large extent, giving a hexose, $C_6H_{12}O_6$. During this operation, a small quantity of crystalline substance was often observed in the exit tube of the apparatus employed, but the quantity was too minute for thorough examination. By taking certain precautions, the authors now find that this crystalline substance can be obtained in fair quantity, that it is invariably produced in the process referred to, and on examination proves to be pure glycollic aldehyde.

Molecular weight determinations by the cryoscopic method indicate that, in the crystalline state, the substance is probably bimolecular, the numbers obtained when the solution is first made approximating to those required for the double formula $C_4H_8O_4$. But on allowing the solution to stand, this value diminishes, and, after about 24 hours, becomes constant, and agrees almost exactly with that required for

the single formula. This behaviour is quite analogous to that which Wöhl observed in the case of crystalline glyceraldehyde (*Ber.*, 1898, 31, 2394).

***64. "On the blue salt of Fehling's solution and other cuprotartrates." By Orme Masson and B. D. Steele.**

In this paper, electrolytic and chemical experiments are described which prove (*a*), that the blue salt contains a complex negative radicle of which copper is a part; (*b*), that none of the copper plays an electropositive part; (*c*), that when a current passes through the blue solution, copper is deposited on the cathode by secondary action of the K ions there; (*d*), that the blue solution may be prepared perfectly neutral to litmus by the interaction of cupric tartrate and alkali in the ratio of 5KOH to $4CuC_4H_4O_6$, and that this neutral solution contains $K_2C_4H_4O_6$ as well as the blue salt; (*e*), that the latter may be completely purified by precipitating it with alcohol; (*f*), that when dried in vacuo it has the composition $K_2C_{12}H_9Cu_4O_{19},4H_2O$; (*g*), that it gives rise to the production, by double decomposition, of a series of salts of the heavy metals, obtained as more or less insoluble, blue, amorphous precipitates, of which the silver and lead salts have been analysed; (*h*), that the free acid corresponding to these cuprotartrates is unstable and, so far, unobtainable; (*i*), that excess of alkali converts the neutral blue cuprotartrate into a strongly alkaline salt, which is also capable of being separated by alcohol.

Discussion.

Dr. Thorne said the blue salt has been recently examined in his laboratory by his assistant, Mr. E. H. Jeffers. It had been obtained by precipitation as a viscid liquid gradually depositing crystals, but it had not yet been isolated in a pure state. It was readily soluble in water, and the aqueous solution did not show any decomposition on boiling.

It is remarkable that the whole of the copper should be present in the negative condition. The complicated formula assigned to the salt seemed improbable, as Luff has recently (*Zeits. ges. Brauw.*, 1898, 21, 319) described a potassium cupric citrate, $K_2Cu(C_6H_4O_7),6H_2O$, obtained in an analogous way. This latter salt appears to be an ordinary double salt with the copper in the positive condition, but its behaviour with reducing sugars is similar to that of the tartrate described.

***65. "The preparation of acid phenolic salts of dibasic acids." By S. B. Schryver, D.Sc., Ph.D.**

When the sodium salt of a phenol is treated with the anhydride of an organic dibasic acid in the presence of a liquid, such as a hydrocarbon, which exerts no chemical action on either the phenol sodium salt or the anhydride, a reaction takes place, which may be represented by the following general equation:—$R\langle^{CO}_{CO}\rangle O + XONa = R\langle^{COOX}_{COONa}$, where R = residue of an organic dibasic acid, X = a phenylic group.

The hydrocarbon most generally employed was xylene. The phenol was dissolved in about ten times its weight of the hydrocarbon, and the sodium salt prepared by the direct action of metallic sodium on this solution. On adding the anhydride, an immediate action takes place in most cases, and the sodium phenolic salt separates out on standing in the form of a gelatinous mass. This can be dissolved up in water and thus separated from the hydrocarbon, and the acid phenolic salt can be precipitated from the aqueous solution of the sodium salt thus obtained by the addition of dilute mineral acids. By means of the reaction, the following substances were prepared:—

Phenol hydrogen camphorate, $CO_2H\cdot C_8H_{14}\cdot CO_2(C_6H_5)$, m. p. 100°. Thymol hydrogen succinate, $CO_2H\cdot C_2H_4\cdot CO_2(C_{10}H_{14})$, m. p. 121—122°. Thymol hydrogen phthalate, $CO_2H\cdot C_6H_4\cdot CO_2(C_{10}H_{14})$, m. p. 132·5°, Thymol hydrogen camphorate, $CO_2H\cdot C_8H_{14}\cdot CO_2(C_{10}H_{14})$, m. p. 89°. Guaiacol hydrogen succinate, $CO_2H\cdot C_2H_4\cdot CO_2(C_6H_4\cdot OCH_3)$, m. p. 75°. Guaiacol hydrogen camphorate, $CO_2H\cdot C_8H_{14}\cdot CO_2(C_6H_4\cdot OCH_3)$, m. p. 112°, from which the neutral salt, $C_8H_{14}(CO_2C_6H_4\cdot OCH_3)_2$, m. p. 124°, was prepared, β-Naphthol hydrogen camphorate, $CO_2H\cdot C_8H_{14}\cdot CO_2C_{10}H_7$, m. p. 120—121°. Eugenol hydrogen camphorate, m. p. 115·5°. Carvacrol hydrogen camphorate, a syrup.

As will be seen from the above examples, the reaction is applicable to a large number of phenols and acid anhydrides, but it does not apply, however, universally. So far, two classes of exceptions have been discovered amongst substituted phenols.

(1). The ortho- and para-nitrophenols.—Whereas the sodium salt of metanitrophenol dissolves readily in a 10 per cent. solution of camphoric anhydride in xylene, neither the corresponding ortho- nor para-compounds react, even when heated to 180° in a sealed tube. Reference is made to the differences in the reactions of meta-compounds, as opposed to the corresponding ortho- and para-compounds, in the publications of Menschutkin (*Ber.*, 1897, 30, 2968) and Lobry de Bruyn (*Rec. Trav. Chem.*, 1894, 13, 101—147). The metanitrophenol camphorate, $CO_2H\cdot C_8H_{14}\cdot CO_2C_6H_4\cdot(NO_2)$, prepared by the reaction,

commences to melt at 115°, but is not completely molten till some degrees higher.

(2). Diortho-substituted phenols.—A series of bromo-compounds was prepared, viz., *p*-bromophenol, 2 : 4-dibromophenol, 2 : 6-dibromophenol, 2 : 4 : 6-tribromophenol. 2 : 6-Dibromophenol was obtained by the reduction of 2 : 6-dibromoparanitrosophenol (OH = 1) and subsequent replacement by hydrogen of the amino-group in the product thus obtained by means of ethyl nitrite. The other bromophenols were obtained by direct bromination.

It was found that, whereas *p*-bromophenol and 2 : 4-dibromophenol readily reacted with camphoric anhydride yielding camphorates, $CO_2H \cdot C_8H_{14} \cdot CO_2C_6H_4Br$ and $CO_2H \cdot C_8H_{14} \cdot CO_2C_6H_3Br_2$, melting respectively at 111° and 173°, neither the 2 : 6-dibromophenol nor the 2 : 4 : 6-tribromophenol reacted, even when heated to 180° in a sealed tube. This non-reactivity is analogous to the non-formation of alkyl salts of diortho-substituted benzoic acids (compare V. Meyer and Sudborough, *Ber.*, 1894, **27**, 510, 512, 1580, 3146). V. Meyer ascribes the non-reactivity to stereochemical causes. In this case, as well as in the reactions described above, it seems doubtful whether the non-reactivity is to be ascribed to the presence merely of two substituted groups in the ortho-position (stereochemical causes), or to the close proximity of two strongly negative groups—in other words, to statical or dynamical causes—especially when the fact is taken into account that even certain mono-substituted products are incapable of reacting.

Discussion.

Dr. Lapworth thought that Dr. Schryver's observations afforded further evidence in favour of the view that in the salts of ortho- and para-nitrophenols the constitution of the nucleus is no longer benzenoid, but quinonoid; that is to say, that the salts are derivatives of iso-nitro-compounds analogous to quinoneoximes, and not to true phenols. In the case of metanitrophenol, as the migration of the phenolic hydrogen into the nitro-group is not possible, and as nitrobenzenes do not form salts, it is probable that the salts of metanitrophenol are true phenolates.

66. "The maximum pressure of naphthalene vapour." By R. W. Allen, M.A.

An accurate knowledge of the amount of naphthalene required to saturate a given volume of gas at various temperatures is of great importance to gas engineers. The author has therefore determined

the vapour pressure of naphthalene both by the "evaporation" and the "barometric" methods, and obtained results which are in entire accord, but which differ notably, especially at the lower temperatures, from the few measurements given by Naumann. The paper contains tables giving the pressures obtained by both methods as well as one giving the weight of naphthalene required to saturate a cubic metre of gas at temperatures varying from 0° to 130°.

67. "Scoparin." By Arthur George Perkin.

Scoparin, the colouring matter of broom (*Spartium Scoparium L.*) was discovered by Stenhouse (*Annalen*, 1851, **78**, 17), who assigned to it the provisonal formula $C_{21}H_{22}O_{10}$ (mean of analyses, C = 57·67; H = 5·34). Hlasiwetz (*Annalen*, 1866, **138**, 190) included scoparin in the quercetin group, for, on fusion with alkali, it gave phloroglucinol and protocatechuic acid.

The similarity of the dyeing properties of scoparin and vitexin pointed to their close relationship (*Trans.*, 1898, **73**, 1019). The results of Stenhouse and Hlasiwetz (*loc. cit.*) have been confirmed as analysis gave C = 57·60, H = 5·09, and fusion with alkali at 220°, phloroglucinol and protocatechuic acid. Digested with hydriodic acid, one molecule of methylic iodide is evolved (found, CH_3 = 3·88), and a new colouring matter, *scoparein*, results, distinguished from scoparin by its strong tinctorial properties. With boiling potassium hydrate solution, scoparin gives phloroglucinol, vanillic acid, and a third substance, $C_9H_{10}O_3$ (found, C = 64·82; H = 6·17), colourless needles m. p. 114°. As this latter contains one methoxy-group (found, CH_3 = 9·65), reacts with semicarbazide, and on fusion with alkali gives protocatechuic acid, it is a *dihydroxyacetophenonemonomethyl ether* (probably OH : OCH_3 : $COCH_3$ = 1 : 2 : 4).

Solutions of vitexin and scoparin in sulphuric acid, when heated, both develop a dull green coloration. The former, by decomposition with alkali, gives *p*-hydroxyacetophenone and phloroglucinol, and it is thus very probable that scoparin is a *methoxy-vitexin*. The author intends to investigate this colouring matter further.

68. "On a new compound of arsenic and tellurium." By E. C. Szarvasy, Ph.D., and C. Messinger, Ph.D.

Whilst investigating the compounds which arsenic forms with the elements of the oxygen group, a regularity in their properties was observed, which led to the discovery of a new telluride. The investigation aimed chiefly at a study of the behaviour of these compounds

at high temperatures, and the determination of their molecular weights by means of their vapour densities.

Selecting from each group of the compounds examined those most stable at high temperatures, a certain numerical regularity was observed between their molecular weights. In the series of compounds having the formulæ As_2O_3, As_2S_3, As_2Se, the differences between the molecular weights of such a series are 16 and 15 units respectively. Similarly, we may determine the formula of the next probable tellurium compound higher in the series, having the same difference between it and the preceding member. Calculation indicated the formula of this compound to be As_8Te_3. It was subsequently prepared by melting its components together in the ratio 8As : 3Te in a sealed tube under pressure. The vapour density of this compound was also determined. The paper concludes with a comparison of the properties of the compounds which arsenic forms with the various elements of the oxygen group.

69. "The action of hydrogen peroxide on secondary and tertiary aliphatic amines. Formation of alkylated hydroxylamines and oxamines." By Wyndham R. Dunstan and Ernest Goulding.

In a previous communication (*Proc.*, 1899, **15**, 58), the authors have shown that methyl iodide reacts with hydroxylamine, forming *trimethylamine oxide* or *trimethyloxamine*, $(CH_3)_3N{:}O$, whilst ethyl iodide forms first *β-diethylhydroxylamine*, $(C_2H_5)_2NOH$, and by further action *triethyloxamine*, $(C_2H_5)_3N{:}O$.

The constitution of these oxamines suggested the possibility of their formation from the corresponding amines by the action of weak oxidising agents. The authors find that trimethylamine is readily oxidised in aqueous solution by standing in the cold with a dilute solution of hydrogen peroxide, forming *trimethyloxamine* identical in properties with the compound already described. Similarly, triethylamine is readily oxidised to *triethyloxamine*. In both cases, the yield is nearly quantitative. Diethylamine, under the same conditions, is converted into *β-diethylhydroxylamine* identical with the compound prepared by the authors by the reaction of ethyl iodide with hydroxylamine. Experiments are now being made with other amines and with ammonia.

70. "The enantiomorphously related tetrahydroquinaldines." By William Jackson Pope and Stanley John Peachey.

Dextrotetrahydroquinaldine was obtained by Ladenburg (*Ber.*, 1894, **27**, 77) by crystallising the externally compensated base with

tartaric acid, when dextrotetrahydroquinaldine bitartrate is eventually obtained in a state of purity. Lævotetrahydroquinaldine has not previously been prepared.

On dissolving externally compensated tetrahydroquinaldine in hot water by addition of a half-molecular proportion each of hydrochloric and dextro-α-bromocamphorsulphonic acids and allowing to cool, *lævotetrahydroquinaldine dextro-α-bromocamphorsulphonate*, $C_{10}H_{13}N,C_{10}H_{14}BrO\cdot SO_3H$, separates in almost quantitative yield. The salt is sparingly soluble in water, and is purified by two or three recrystallisations from alcohol; it crystallises in colourless needles melting at 218—220°, and on treatment with soda the base separates as an oil, which is extracted with ether and purified by distillation under reduced pressure.

Lævotetrahydroquinaldine, $\begin{matrix}CH{:}CH\cdot C\cdot CH_2\cdot CH_2\\ CH{:}CH\cdot C\cdot NH\cdot CHMe\end{matrix}$, is a colourless, highly refractive oil of faint basic odour, and boils at 158° under 59 mm. pressure. It has a specific gravity of 1·0236 at 14·5°/4°, and gives the rotation $\alpha_D = -58{\cdot}60°$ in a 100 mm. tube at 16°; the specific rotation is therefore $[\alpha]_D = -57{\cdot}25°$. For the rotations of the dextro-isomeride, Ladenburg gives $\alpha_D = +58{\cdot}35°$ and $[\alpha]_D = +55{\cdot}99°$, having apparently used the density of the externally compensated base in calculating the specific rotation.

Benzoyl-lævotetrahydroquinaldine, $C_{10}H_{12}N\cdot COPh$, is readily obtained, by shaking the base with dilute soda and benzoyl chloride, as a granular crystalline mass, which is purified by crystallisation from ethyl acetate. It separates from cold acetone in lustrous colourless monosymmetric prisms melting at 117—118°, and has the specific rotation $[\alpha]_D = +247{\cdot}3°$ in a 3·5 per cent. benzene solution. A comparison of its properties with those of Walter's optically inactive benzoyltetrahydroquinaldine (*Ber.*, 1892, **25**, 1261) shows that the latter is a true racemic compound.

After filtering off the lævotetrahydroquinaldine dextro-α-bromocamphorsulphonate, the mother liquor is made alkaline, and the crude dextrotetrahydroquinaldine extracted with ether, and converted into dextrocamphorsulphonate by addition of the requisite quantity of Reychler's camphorsulphonic acid (*Bull. Soc. Chim.*, 1898, [iii], **19**, 120); a crystalline substance separates which, after repeated recrystallisation from acetone, yields *dextrotetrahydroquinaldine dextrocamphorsulphonate*, $C_{10}H_{13}N,C_{10}H_{15}O\cdot SO_3H$. This salt crystallises in colourless needles melting at 127—128°, and has the specific rotation $[\alpha]_D = +45°$ in a 4 per cent. aqueous solution; it yields Ladenburg's dextrotetrahydroquinaldine when treated with soda. *Lævotetrahydroquinaldine dextrocamphorsulphonate*, $C_{10}H_{13}N,C_{10}H_{15}O\cdot SO_3H$, also crystallises well,

separating from acetone solution in long, colourless needles melting at 137—138°; it has the specific rotation of $[\alpha]_D = -16°$.

Benzoyldextrotetrahydroquinaldine, $C_{10}H_{12}N \cdot COPh$, is completely analogous to its enantiomorphously related isomeride; it melts at 117—118° and has the specific rotation of $[\alpha]_D = -247{\cdot}4°$ in a 4 per cent. benzene solution. The benzoyl derivatives now described are hydrolysed by prolonged boiling with hydrochloric acid, yielding benzoic acid and the original base.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in June. Application for Grants, to be made on forms which can be obtained on application to the Assistant Secretary, must be received on or before May 31st.

COLLECTIVE INDEX.

Fellows can obtain the Collective Index 1873—1882 from the Assistant Secretary at the price of 10*s.*, or 11*s.* including carriage. The price of the Collective Index 1883—1892 to Fellows is 16*s.* including carriage.

At the next meeting, on May 18th, the following papers will be communicated by the authors:—

"Corydaline. Part VI." By J. J. Dobbie, Ph.D., and A. Lauder.

"Oxidation of furfurol by hydrogen peroxide." By C. F. Cross, E. J. Bevan, and T. Freiberg.

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May 18th, 1899. Professor Thorpe, F.R.S., President, in the chair.

Messrs. H. H. Bowles, F. S. Young, and R. Haliburton Adie were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. George Dekeyne Atkinson, c/o Crowley and Co., The Brewery, Alton, Hants; James Connah, Geralton, Carlton Road, Sidcup; Robert McClumpha, 372 Westgate Road, Newcastle-on-Tyne; Eskricke Sidney Phillips, Christ's College, Cambridge; John William Shepherd, 48 Ovington Street, S.W.; Charles Simmonds, 17 Ruvigny Gardens, Putney, S.W.

Of the following papers, those marked * were read.

***71. "Corydaline. Part VI." By James J. Dobbie and Alexander Lauder.**

In this paper, the authors give the results of the investigation of *corydaldine*, $C_9H_7NO(OCH_3)_2$, one of the substances obtained by the oxidation of corydaline by means of potassium permanganate (*Trans.*, 1894, 65, 57). By employing a smaller proportion of permanganate and using it at the ordinary temperature, a larger yield was obtained than by the method previously described.

Corydaldine readily dissolves in water, melts at 175°, and contains two methoxyl groups. Dissolved in hydrochloric acid and treated with sodium nitrite at 0°, a yellow nitroso-derivative is obtained (m. p. 185°), which is very insoluble in hot and cold water. When this nitroso-derivative is gently warmed with a solution of sodium

hydrate, nitrogen is evolved, and on addition of hydrochloric acid to the solution a new substance, melting at 138—139°, is obtained, which is the anhydride of a monobasic acid. Its formula is $C_{11}H_{12}O_4$; it is difficultly soluble in cold but readily in boiling water, from which it crystallises well on cooling. Treatment with hydrogen iodide proves that it contains two methoxyl groups, and oxidation with permanganate at 100° converts in into metahemipinic acid. Heated with hydrochloric acid at 150°, a phenolic derivative (m. p. 232°) is obtained, which shows all the reactions of ω-hydroxyethylcatecholcarboxylic anhydride obtained by Perkin from berberine (*Trans.*, 1890, 57, 1028). The authors therefore conclude that *corydaldine* only differs from ω-amidoethylpiperonylcarboxylic anhydride in having two methoxyl groups instead of the piperonyl group, and that it is closely related to oxy-hydrastinine.

Corydaline is thus proved to be closely related to berberine, hydrastine, narcotine, and papaverine, in common with which it contains an isoquinoline nucleus. When the alkaloid is oxidised at 100° by means of potassium permanganate, the chief product is a mixture of hemipinic and metahemipinic acids.

The substance previously described under the name of corydalinic acid (*Trans.*, 1894, 65, 57) is found to be an acid ammonium salt of metahemipinic acid, having the formula $C_{10}H_{10}O_6,C_{10}H_9O_6(NH_4),3H_2O$.

***72. "Oxidation of furfural by hydrogen peroxide." By C. F. Cross, E. J. Bevan, and T. Heiberg.**

The results described in this paper are obtained by interaction of the aldehyde and peroxide in dilute aqueous solution (2—4 per cent. furfural) at 40° in presence of iron salts in small quantity. The peroxide is added until the characteristic reaction of the aldehyde with aniline acetate is no longer obtainable, the quantity of peroxide required being two to three molecules per molecule of furfural.

The main product of oxidation is recognised by its reactions with phenylhydrazine (formation of hydrazone), and with phloroglucinol and hydrochloric acid (deep red-violet coloration followed by precipitation of the colouring matter) to be a furfural derivative. Analysis of the hydrazone shows it to be the hydrazine derivative of a *hydroxyfurfural*. Along with this main product is an acid, which is easily separated as a barium salt insoluble in acetic acid. Analyses of the barium and lead salts show the acid to be the corresponding *hydroxypyromucic* acid.

The substitution of hydroxyl for hydrogen in the furfurane nucleus agrees with the results of previous investigations as to the mode of action of the peroxide; but, as a further confirmation, its action

on benzene under conditions similar to those in the above described experiments has been so far studied as to prove the formation of a considerable quantity of phenol. The furfural-phenol corresponds to an oxybenzaldehyde; reasons are given for regarding the OH and CHO-groups as occupying the 1 : 2-positions. It is noteworthy that, as in the case of the normal saturated "carbohydrates," the CHO-group is but slowly attacked by the peroxide relatively to a CH-group.

The further action of the peroxide is destructive in character, the furfurane ring being broken down, the chief product being formic acid, along with some acetic and oxalic acids. The intermediate products appear from their reactions to be hydroxyketonic acids. The formation of methylated compounds is probably a secondary result of the decomposition; from the products of the original reaction, iodoform is obtainable in some quantity, and the amounts have been estimated.

Special interest attaches to the hydroxyfurfural which has been thus obtained. Its reactions with phloroglucinol and with resorcinol in presence of HCl are similar to those of the lignocelluloses. These colours may be developed on a pure cellulose cloth or paper for comparative study. It is then seen that the brilliant colours of the original products—blue with resorcinol, violet with phloroglucinol, give place to "flattened" shades, grey and brown respectively, on washing with ordinary water.

By means of these reactions, it is now shown (1) that a furfural-phenol is a constituent of the lignocelluloses; (2) that the colour reactions of these 'natural' products with the hydroxybenzenes are due to the presence of such compounds; (3) that the equally characteristic reactions of the lignocelluloses with aniline salts are reactions with a second constituent group, *e.g.*, the keto-R-hexene complex.

A furfural-phenol being a normal product of the condensation processes accompanying lignification, it is probably also a product of the action of the condensing acids used in estimations of furfural. It appears, therefore, that the furfural actually isolated does not necessarily represent the entire production of furfurane derivatives; and these observations supply the basis for a further differentiation of the complex group of furfural-yielding plant constituents or furfuroids.

Discussion.

Mr. F. S. Young said that, as the result of some preliminary experiments, he had found that, although hydrogen peroxide by itself attacks benzene only very slowly, an extremely energetic reaction takes place in the presence of ferrous salts. A complete examination of the products of the reaction has still to be made; but he had proved that a considerable quantity of phenol is formed.

In two preliminary experiments, in which one molecule and two molecules of hydrogen peroxide were used for one molecule of benzene, the yield of phenol was 10 per cent. and 20 per cent. respectively; and it is possible that this yield may be increased when the most favourable conditions for its formation have been determined. Pyrocatechol was also obtained as a product of the reaction.

Mr. FENTON said that the results obtained by Messrs. Cross and Young with furfural and benzene, together with those which had been observed by himself and others in the case of phenol, appeared to establish a third typical reaction of hydrogen peroxide in presence of iron—namely, the replacement of hydrogen by hydroxyl.

With reference to Mr. Cross's suggested explanation of the mechanism of the reaction, he did not think that it was applicable to the cases which he (Mr. Fenton) had studied, since other oxidising agents might be substituted for the hydrogen peroxide.

Mr. CROSS, in reply, said, with regard to the mechanism of the action of hydrogen peroxide, that although the tendency of the peroxide to split into hydrogen and oxygen might not be suggested by its interactions with inorganic compounds, yet its behaviour with carbon compounds, especially those which are unsaturated, might furnish evidence of such intermediate phases as would disappear in the final stages of the reaction.

***73. "Note on the reactions between sulphuric acid and the elements." By R. H. Adie.**

The publication of a paper by M. Berthelot on the action of sulphuric acid on metals (*Ann. Chim. Phys.*, 1898, [vii], **14**, 176—204), leads the author to publish the results of some experiments which he performed some years ago. The results obtained by Berthelot in the case of zinc confirm those of Muir and the author (*Trans.*, 1888, **53**, 47), and in the case of copper, those of Pickering (*Trans.*, 1878, **33**, 112). In the following table, the temperatures of decomposition of sulphuric acid by the easily obtainable elements are given, these being grouped according to the periodic system.

It appears possible, even at this stage, to draw a few conclusions.

(i) Sulphuric acid is decomposed by most elements, with the formation of sulphur dioxide and hydrogen. Sulphuretted hydrogen only appears as a special impurity in a few cases.

(ii) In any group of elements, the decomposition temperature becomes lower as the atomic weight of the element increases.

(iii) Copper, nickel, and palladium all form black sulphides, and also all give compounds with ammonia.

(iv) In the case of zinc, a pure specimen (kindly given by Professor Ramsay) caused the temperature of decomposition to rise to 250°. With this specimen, no hydrogen sulphide was evolved up to the boiling point of the acid. This suggests the unsuitability of ordinary zinc for further work.

Element.	SO_2 appears.	H_2S appears.	Notes.
Hydrogen ...	170°	None.	Gas prepared from Zn and HCl washed and dried with H_2SO_4.
Copper	Begins 110—115° Continuous 120°	None.	Cu_2S formed.
Silver	175°	None.	Gas evolved at 150°.
Magnesium...	215°	Trace.	
Zinc.....	250°	None.	SO_2 evolved as soon as reaction starts.
Cadmium	205°	Trace ?	
Mercury	120°	None.	Gas given off at 110°.
Aluminium...	235°	None.	No bubbles of SO_2.
Carbon.....	188°	None.	
Tin	145°	None.	S formed.
Lead	140°	None.	
Thallium.....	Below 20°	Below 20°.	Formed at once at ordinary temperature. Brown solid formed.
Arsenic	110°	None.	No AsH_3.
Antimony ...	90—95°	None.	
Bismuth	90°	None.	Gas evolved at once.
Sulphur	200°	None.	Melts at 220° No bubbles till 230°.
Selenium.....	170°	None.	
Molybdenum.	135°	None.	Gas begins at 115°. Green solid formed.
Tungsten	175°	None.	
Manganese ...	155°	None.	Gas evolved at 120°.
Iodine	—	—	Passes over at 92°. No action before.
Iron.....	220°	None.	Gas evolved at 170°.
Nickel	145°	None.	Black solid formed.
Cobalt	240°	None.	
Palladium ...	200°	None.	Reaction not vigorous. Blackens from formation of sulphide.
Platinum	None.	None.	

The author intends to make a fuller investigation of some of the more definite reactions.

74. "On the action of ethylene dibromide and of trimethylene dibromide on the sodium derivative of ethylic cyanacetate." By H. C. Harold Carpenter and William H. Perkin, jun.

One of the great difficulties in investigating the derivatives of trimethylene is the fact that the condensation of ethylene bromide with the sodium compounds of ethyl malonate and ethyl acetoacetate gives only a very small yield of trimethylene compounds (*Trans.*, 1885, 47, 808); and again, in investigating the formation of tetramethylene compounds by the action of trimethylene bromide on the

sodium derivative of ethyl malonate, the best yield of ethyl tetramethylenedicarboxylate (1,1) obtained was only 33 per cent. (*Trans.*, 1887, 51, 3).

It appeared to us possible that the yield of these closed-chain compounds might be considerably increased if ethyl cyanacetate was substituted for ethyl malonate and acetoacetate, and this has been found to be the case.

Ethyl trimethylenecyancarboxylate (1,1), $\begin{matrix}CH_2\\CH_2\end{matrix}\!>\!C\!<\!\begin{matrix}CN\\CO_2Et\end{matrix}$, of which 50—60 per cent. is obtained by the action of ethylene bromide on the sodium derivative of ethyl cyanacetate, is a colourless, mobile liquid, boiling at 210—211° under 766 mm. pressure, $\Delta^{0°}_{4°}=1{\cdot}0783$. It dissolves gradually in aqueous ammonia (sp. gr. = 0·88) forming the amide, which crystallises in lustrous needles (m. p. 160°). Cold methyl alcoholic potash saponifies it instantly, with the production of the potassium salt of *trimethylenecyancarboxylic acid* (1,1). The acid is obtained in the form of long, colourless prisms by the evaporation of its ethereal solution in a stream of dry air. It melts undecomposed at 148°. It is remarkable that all attempts to split off the carboxyl group and prepare cyantrimethylene, (i) by distilling the acid, (ii) by heating it in sealed tubes with a small quantity of water, (iii) by heating the silver salt, have failed. Recently, however, this substance has been prepared by L. Henry, who distilled γ-chlorbutyronitrile repeatedly over solid potash and obtained it in the form of a colourless liquid of pleasant odour. B. p. = 135°, $\Delta^{16°}=0{\cdot}911$ (*Bull. Acad. roy. Belgique*, 1898, [iii], **36**, 34; 1899, [iii], **37**, 17—22).

The silver salt is a very characteristic substance. It is soluble in water, and crystallises from its aqueous solution in lustrous prisms. The conversion of the trimethylenecyancarboxylic acid into trimethylenedicarboxylic acid is best effected by boiling with aqueous potash. From the latter acid, its characteristic derivative, bromethylmalonic acid (m. p. 116°) was prepared by the action of aqueous hydrobromic acid (sp. gr. = 1·83).

The condensation of ethylene bromide with the sodium derivative of ethyl cyanacetate yields, besides the trimethylene derivative, two crystalline substances, the one melting at 119°, the other at 95—96°, according as the reaction is made to take place under pressure in soda-water bottles or at ordinary pressures. These substances have been analysed, but their constitutions have not yet been discovered.

Ethyl tetramethylenecyancarboxylate (1,1), $\begin{matrix}CH_2—CH_2\\CH_2—C(CN)\cdot CO_2Et\end{matrix}$, is obtained to the extent of 60—70 per cent. by the action of trimethylene bromide on the sodium derivative of ethylcyanacetate. It is a colourless liquid boiling at 213—214° under 766 mm. pressure, $\Delta^{0°}_{4°}=1{\cdot}0633$.

It dissolves in aqueous ammonia (sp. gr. = 0·88), but the resulting amide is easily soluble and does not crystallise out. Cold methyl alcoholic potash saponifies it at once, forming the potassium salt of *tetramethylenecyancarboxylic acid* (1,1). The free acid is purified by crystallisation from carbon disulphide containing a small quantity of ether, and is thus obtained in long, silky needles, which have the remarkably low melting point 69—70°. By careful heating, they may be sublimed unchanged. The silver salt is completely analogous to that of the corresponding trimethylene acid. Boiling aqueous potash hydrolyses the cyanogen group, and the product is tetramethylenedicarboxylic acid (1,1), which melts at 157°. The characteristic lead salt was prepared and analysed. The by-product in the preparation of the ethyl tetramethylenecyancarboxylate is an oil. The investigation of this substance is in progress.

75. "The maximum vapour pressure of camphor." By R. W. Allen, M.A.

By the two methods which he employed in determining the vapour pressures of naphthalene (*Proc.*, 1899, **15**, 122), the author has determined the maximum pressures of camphor vapour from 0—80°. The results obtained by these methods agree throughout, but differ very notably from those obtained by Ramsay and Young (*Phil. Trans.*, 1884, **175**, 45).

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

The following Candidates have been proposed for election. A ballot will be held on Thursday, June 15th, 1899.

Aders, Robert Henry,

28, St. John's Wood Road, N.W.

Student, University College, London. Student for B.Sc. Lond. Exam., and have worked since October, 1897, in Chemical Laboratory, University College, London.

William Ramsay.	A. M. Kellas.
Morris W. Travers.	G. Nevill Huntly.

S. Smiles.

Atkinson, George Dekeyne,

c/o Crowley and Co., The Brewery, Alton, Hants.

Brewer. Medical, passed in Chemistry in 1882, London; Member of the Institute of Brewing since foundation; Member of the Belgian Association of Chemists; studied Chemistry of Brewing in Technical Laboratory. Fifteen years' Brewing experience, and interested in the Biological and Chemical Research work connected therewith.

Chas. Geo. Matthews.	Horace T. Brown.
George Harrow.	G. Harris Morris.
Jas. O'Sullivan.	John Heron.

Adrian J. Brown.

Bean, Percy,

42, Granville Road, Blackburn.

Analytical Chemist. Lecturer on "Textile Chemistry" at the Harris Institute, Preston, and the Darwen Technical School, and late Lecturer on Inorganic and Textile Chemistry at Blackburn ditto. Author of "The Origin, Development, and Classification of Iron Stains in Cotton Cloth." First Classes at South Kensington Examinations in

both Advanced Inorganic Theory and Advanced Practical Inorganic Chemistry.

Edward Davies. E. Haworth.
C. Gerland. Wm. Hall Jowett.
J. W. Clayton.

Blackman, Walter Lionel,

Mostyn, Mount Nod Road, Streatham, S.W.

One year General Science at St. Bartholomew's Hospital; 2½ years Chemistry, Organic and Inorganic, at the Royal College of Science, London. Since then research work at St. Bartholomew's Hospital.

W. J. Russell. W. Palmer Wynne.
William A. Tilden. F. D. Chattaway.
K. J. P. Orton.

Carpmael, Wilfred,

24, Southampton Buildings, Chancery Lane.

Chartered Patent Agent. I was from October, 1885, to August, 1887, a Student of Chemistry at the University of Berlin under Prof. A. W. von Hofmann, and have for the past 12 years had great experience in drawing chemical specifications and discussing chemical inventions with inventors, having during the first part of that time been in the employment of, and recently a member of, the firm of Carpmael and Co.

James Dewar. R. Meldola.
Alfred Gordon Salamon. Walter F. Reid.
F. E. Allhusen.

Connah, James,

Geralton, Carlton Road, Sidcup.

Analyst in the Goverment Laboratory. B.Sc. (Lond.) (Honours, Chemistry); F.I.C.; Student in Chemistry, Royal College of Science, 1884—1885; Lecturer in Agricultural Chemistry at City of London College and Birkbeck Institution, 1890—1893.

T. E. Thorpe. C. Proctor.
H. J. Helm. J. Woodward.
E. Grant Hooper. J. H. Robbins.

Danziger, Henry Meldola,

Cleut House, Woodland Road, Northfield, Birmingham.

Chemist. Student in the Owens College Laboratories for four years. Chemist to the King's Norton District Council.

J. Carter Bell. H. B. Dixon.
William A. Bone. W. H. Perkin, jun.
G. H. Bailey.

Doyle, Frederick,
8, Woodlands Terrace, Middlesbrough.
Science Teacher. Lecturer on Chemistry for the last four years at Middlesbrough High School.

J. G. Taylor.	J. Archyll Jones.
Wm. Goddard.	*Duncan T. Richards.*

William Lewins.

Dunscombe, Frederick Charles,
54, Woodstock Road, Bristol.
Analytical Chemist. Three years' course Merchant Venturers' School, Applied Science Department; Second Class Honours Practical Inorganic Chemistry, Intermediate Honours Practical Metallurgy, Advanced Stage Theoretical Inorganic Chemistry and Metallurgy (all at South Kensington Examinations); three years Assisant at the Clifton Laboratory, Bristol.

Ernest H. Cook.	George George.
Henry J. Palmer.	*Arnold Philip.*
James Leicester.	*Sydney Young.*

G. P. Darnell-Smith.

Eichenauer, William Frederick,
58A, Maryon Road, Old Charlton, Kent.
Analytical Chemist and Electrican. Chief Assistant in the Laboratory of Messrs. Siemens Brothers and Co. for 18 years. Have had considerable experience in Analytical and Electrochemical work. Assisted the late Dr. Obach in carrying out his well-known researches on gutta percha and indiarubber.

Henry Durham.	Thomas Bolas.
Isaac S. Scarf.	*W. Kellner.*

Herbert Jackson.

Fleischmann, Friedrich Noel Ashcroft,
6, Collingham Gardens, South Kensigton, London; Magdalen College, Oxford.
Undergraduate of Magdalen College, Oxford. Student in Honour School of Natural Science (Chemistry).

Henry A. Miers.	J. E. Marsh.
John Watts.	G. Stallard.
H. L. Bowman.	W. W. Fisher.

E. G. J. Hartley.

Fraser, William Gordon,
Golspie, St. Albans.
Chemical Student. Have studied Chemistry at the City and Guilds

Technical College (under Professor Meldola) and obtained the College Certificate in Organic Chemistry (Evening Classes). Have devoted some considerable time to the investigation and analysis of fats and oils.

R. Meldola. A. Hall.
Arthur J. Chapman. *Arthur Ross.*
R. L. Jenks.

Getman, Frederick Hutton,

196, Atlantic Street, Stamford, Conn., U.S.A.

Analytical Chemist. Assistant in Physics at Rensselaer Polytechnic Institute in 1895. Graduate of School of Analytical and Industrial Chemistry, University of Virginia; Assistant Editor of *Popular Science News*, New York (Department Physics and Chemistry); member American Chemical Society, Society Chemical Industry, American Association Advanced Science; Chemist to Berkshire Portland Cement Company.

Chas. Baskerville. F. P. Dunnington.
J. W. Mallet. *F. P. Venable.*
W. H. Chandler.

Hübner, Julius,

24, Delanney's Road, Crumpsall, Manchester.

Chemist and Colourist. Teacher of Bleaching, Dyeing, and Printing and Paper Manufacture. Taught the above subjects for seven years at the Municipal Technical School, Manchester. Thirteen years' experience in Aniline Colour Works, Dye Works (Cotton, Wool, and Silk) and Paper Mill.

John Allan. Alex. K. Miller.
James Grant. *William Thomson.*
George H. Hurst. *Frank Scudder.*

Johnson, Edward Charles,

Lithgow, N.S. Wales, Australia.

Assayer, Great Cobar Copper Mining Company. Over nine years Laboratory Assistant Government Analyst, Tasmania. Assayer, Silver King Mine, Zeehan, Tas. Assayer, Grubb's Silver Mg. Co., Zeehan, Tas. Assayer, Mt. Drysdale Gold Mg. Co., N.S.W. Assayer, The New Eldorado Gold Mg. Co., N.S.W. Investigations made by me *re* loss of silver by concentration of silver lead ore, Tasmanian Secretary of Mines Report, 1894—1895.

William M. Hamlet. James Taylor.
Alexander Orr. *John C. H. Mingaye.*
F. B. Guthrie.

Leon, Arthur Alexander,

13, Cleveland Square, Hyde Park, W.

Brewer. One year Chemistry with the Rev. A. Wentworth Jones, M.A. Two years in a brewery. Six months with Dr. Moritz and Dr. Morris studying special brewing chemistry, and am at present taking a course of Bacteriology at the "Hansen Laboratory" of the "Jenner Institute."

Horace T. Brown. A. Wentworth Jones.
James H. Millar. M. O. Forster.
G. Harris Morris.

McAlley, James,

Bankside, Falkirk.

Analytical Chemist. Studied Chemistry for 3 years with R. R. Tatlock, Readman, and Thomson, City Analysts, Glasgow, and obtained various prizes of value. Subsequently occupied the position of Assistant for about 1 year. At present Head Chemist to the Scottish Cyanide Co., Ltd., Leven, N.B., and have been engaged for the past 4½ years in carrying out Experimental and Research Work in connection with the manufacture of cyanides.

R. R. Tatlock. John Shields.
G. H. Gemmell. William Ramsay.
Geo. W. MacDonald.

McClumpha, Robert,

372, Westgate Road, Newcastle-on-Tyne.

Analytical and Pharmaceutical Chemist. A member of the Pharmaceutical Society of Great Britain. Principal of the West End School of Chemistry, Newcastle, and was for some time Analytical Chemist in charge of the Laboratory of Mawson, Levan, and Weddell, Newcastle. I have had several years' experience as a Teacher and Demonstrator, and at present conduct classes at the above-named West End School of Chemistry.

Edward Davies. Frederick Gilderdale.
C. Ranken. *T. H. Walker.*
Prosper H. Marsden. *P. Phillips Bedson.*

Parkes, George Alfred,

Muckomore Bleach Works, co. Antrim, Ireland.

Chemist (Works). Full Honours Technological Certificates in Bleaching, Dyeing, Printing, and Coal-tar Colours, City and Guilds of London Institute. Practical Honours Chemistry, South Kensington. Until recently Assistant to Dr. E. Knecht in the Dyeing Department of the Manchester Technical School. Lecturer in Calico and Linen Bleaching and Printing at the above schools. Also

Lecturer in Bleaching, Dyeing, and Printing in the Accrington and Middleton Technical Schools. Now appointed Chief Chemist to the York Street Flax Spinning Co., Ltd., Belfast.

Jas. Grant. R. L. Taylor.
John Allan. *C. Rawson.*

Thorp Whitaker.

Peachey, Stanley John,
48, Grange Road, S.E.

Senior Assistant Goldsmiths' Institute, New Cross, S.E. Joint author of following two papers: (1) "The Resolution of Racemic Tetrahydropapaverine" (*Trans. Chem. Soc.*, 1898); (2) "The Non-resolution of Tetrahydropapaverine by Tartaric Acid."

William J. Pope. Sidney Williamson.
Gerald T. Moody. Edwin C. Jee.

T. M. Lowry.

Phillips, Eskricke Sidney,
Christ's College, Cambridge.

School Master. B.A. Cambridge. Natural Science Tripos.
Charles T. Heycock. W. T. N. Spivey.
W. J. Sell. T. B. Wood.

H. J. H. Fenton.

Rossiter, Sidney,
19, Ranelagh Road, West Green, N.

Schoolmaster. Undergraduate of London University. Student at Bath, 1886—1887, under Mr. Gatehouse, F.I.C., public analyst, and for four years at East London Technical College, under Dr. Macnair and Dr. Hewitt. Teacher of Chemistry and Physics at Portman Place Higher Grade School, Mile End, since 1894. Taught Inorganic Chemistry (Science and Art Dept.), and had charge of Laboratory since 1897. Inorganic Chemistry (1st Advanced), Theoretical, 1897; Practical, 1894. Organic Chemistry (1st Ely.), Theoretical, 1898.

W. B. Hards. D. S. Macnair.
Chas. T. F. Watts. W. Mayhowe Heller.

Hugh Gordon.

Royal-Dawson, Henry,
3, Kenilworth Road, Ealing, London, W.

Analytical Chemist. Have received my general experience in Practical and Theoretical Chemistry at University College, Gower Street, W.C., during Sessions 1889—1890, 1890—1891, 1891—1892, after which period have devoted myself to Analytical Chemistry, gaining

experience in the analyses of minerals, food, and water, and am at present engaged on special work under Dr. Clowes.

William Ramsay.	J. H. Coste.
Frank Clowes.	Watson Smith.
R. Grimwood.	*E. Brooks Pike.*

Charles J. S. Makin.

Shepheard, William Frederick John,
12, Bridge Street Row, Chester.

Pharmaceutical and Manufacturing Chemist. Student in the School of the Pharmaceutical Society. Has passed Major Examination of the Society. Subsequently worked in the Research Laboratory of the Pharmaceutical Society. Joint author with Professor Dunstan of paper on "Identity of Caffeine and Theine" (*Journ. Chem. Soc.*, 1893, **63**, 195).

Wyndham R. Dunstan.	Chas. T. F. Watts.
Chas. Umney.	W. F. Lowe.
G. Watmough Webster.	John C. Umney.

Shepherd, John William,
48, Ovington Street, S.W.

Lecturer on Chemistry. Student Glasgow Technical College. Atkinson Scholar, 1889—1892. Student Royal College of Science four years. Associate in Chemistry and in Geology. Bachelor of Science, London University. Various appointments as Science Teacher. Assistant Lecturer Salford Technical Institute.

T. E. Thorpe.	Gilbert T. Morgan.
W. Palmer Wynne.	Chapman Jones.

A. E. Tutton.

Simmonds, Charles,
17, Ruvigny Gardens, Putney, S.W.

Analyst. B.Sc., London. Student at Royal College of Science, 1887—1888. Analyst in Government Laboratory, London, 1888 to present time.

T. E. Thorpe.	J. H. Robbins.
H. J. Helm.	C. Proctor.
E. Grant Hooper.	J. Woodward.

Stainer, John Ward,
103, Cheriton Road, Folkestone.

Pharmaceutical Chemist. Pathological Chemist and Bacteriologist. Student of Yorkshire College, Leeds, 1886—1887. Pupil of Mr. Sidney

Harvey, F.I.C., Canterbury. Revision of Dr. Campbell Black's "Chemistry of Urine" (for publisher).

Arthur Smithells.	W. Lloyd Williams.
Sidney Harvey.	*Francis H. Carr.*
Herbert Ingle.	*Peter MacEwan.*

Stansfield, Samuel,

White Lee, Mytholmroyd, Manchester.

Senior Assistant and Science Instructor in the Pupil Teachers' Centre at the Hebden Bridge Central Schools. Bachelor of Science (Vict.). Associate of the Owens College. Four years student at the Owens College. Lecturer in Chemistry at the Hebden Bridge Science and Technical School.

H. B. Dixon.	G. H. Bailey.
W. H. Perkin, jun.	W. T. Lawrence.

D. S. Jerdan.

West, George Hardstaff,

Frankwell, Llanidloes.

Science Master in the County School, Llanidloes. B.Sc. (Lond.). Honours in Chemistry. Three years student at Mason College, Birmingham. One year student at Royal College of Science, London. Two years Science Master in the County School, Llanidloes.

William A. Tilden.	Charles A. West.
W. Palmer Wynne.	A. E. Tutton.
Chapman Jones.	Edward Russell.

Whittaker, Christopher Joseph,

Willow House, Blackburn Road, Accrington.

Chemical Manufacturer, Globe Chemical Works, Church. Councillor (Accrington Borough). Whitworth Scholar, 1880. Royal Exhibitioner, 1882. Honours, Chemistry, Agriculture, practical plane and solid Geometry, Machine Construction and Drawing, Steam, Applied Mechanics, &c. Teacher of Chemistry, Mathematics, Mechanics, &c., at the Accrington Mechanics' Institution for several years.

Thomas Whittaker, jun.	C. Gerland.
Joshua Bardsley.	Wm. Naylor.

J. H. Calvert.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in June. Application for Grants, to be made on forms which can be obtained on application to the Assistant Secretary, must be received on or before May 31st.

At the next meeting, on Thursday, June 1st, the following papers will be communicated by the authors:—

"The hydrosulphides, sulphides, and polysulphides of potassium and sodium." By W. Popplewell Bloxam.

"On the relative efficiency of various forms of still-head for fractional distillation." By Sydney Young, D.Sc., F.R.S.

"The salts of dimethylpyrone, and the tetravalence of oxygen." By J. N. Collie, Ph.D., F.R.S., and T. Tickle.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 15. No. 211.

June 1st, 1899. Dr. W. H. Perkin, F.R.S., Vice-President, in the Chair.

Messrs. S. Wellington, P. J. D. Fielding, C. R. Darling, and H. M. Read were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. James Dick Dougall, Millom, Cumberland; Ernest Frederick Stephen Lange, Sunny Nook, Victoria Road, Withington, Manchester.

In response to an invitation from the University of Cambridge, the President was delegated by the Council to represent the Society at the Jubilee of Professor Sir G. G. Stokes, and in its name to present the following Address:—

To Sir George Gabriel Stokes, Bart., M.A., D.C.L., LL.D., D.Sc., F.R.S.

We, the undersigned, President and Officers of the Chemical Society, beg, on behalf of the Council and Fellows, to offer you our sincere and hearty felicitations on the occasion of your Jubilee as Lucasian Professor of Mathematics in the University of Cambridge.

The fifty years during which you have held a position so honourable in the ancient University which claims you as among the most distinguished of her sons have witnessed an extraordinary and unprecedented development in those branches of natural knowledge which are immediately connected with the work of your professorship. To this development your own labours as a teacher and an investigator have

contributed in no small degree. You have profoundly influenced the teaching of physics wherever this subject is taught, and this influence has of necessity extended into those departments of Chemical Science which are directly dependent upon, or are associated with, physics. We gratefully acknowledge the services you have rendered to chemical physics by your researches on hydrodynamics, by your contributions to the theory and practice of spectrum analysis, and by your optical investigations. Your memorable contribution to our own Journal, "On the Application of the Optical Properties of Bodies to the Detection and Discrimination of Organic Substances," made more than a third of a century ago, has borne fruit an hundredfold, and to-day the refractometer and the spectroscope are as indispensable to the chemist as is his balance. We are glad to recognise that your interest in our special field of inquiry, springing from that catholicity which is your characteristic, has in no wise abated, for there is hardly a chemical subject bordering upon those branches of physical research which you have made more especially your own that has not been elucidated and benefited by your kindly criticism and advice. There are many workers in our Society who thankfully acknowledge the ready help which you have rendered to them by your counsel and suggestions.

That you may long continue to enjoy, in health and prosperity, the esteem and respect with which you are universally held by those who labour for the advancement of knowledge and the spread of learning, is the heartfelt wish of every member of that body on whose behalf we now address you.

T. E. Thorpe, *President.*
William A. Tilden, *Treasurer.*
Wyndham R. Dunstan, } *Secretaries.*
Alexander Scott, }
Raphael Meldola, *Foreign Secretary.*

Of the following papers, those marked * were read :—

*76. "The hydrosulphides, sulphides, and polysulphides of potassium and sodium." By W. Popplewell Bloxam.

In this paper, the author shows that there is a very important difference between treating the aqueous solution of a sulphide and one of a hydrosulphide with sulphur. When sulphur is added to aqueous solutions of potassium and sodium sulphides, some thiosulphate is always formed along with the polysulphide, whilst hydrogen sulphide is evolved. This points to the sulphide having become, in part at least, hydrolysed into hydroxide and hydrosulphide. The action of sulphur on aqueous solutions of the pure hydrosulphides gives pure polysulphides with evolution of hydrogen sulphide.

The various wet and dry methods of preparing the sulphides and polysulphides of potassium and sodium described by the many authors who have worked at this subject have been repeated by the author, who concludes that (1) none of these authors could have obtained any polysulphide pure, but only a mixture of polysulphide and thiosulphate; (2) no method exists for separating the polysulphide from the thiosulphate.

The author has succeeded in obtaining the following hydrates of potassium sulphide: $K_2S,2H_2O$; $K_2S,5H_2O$; $K_2S,12H_2O$. These salts can be dehydrated in a current of dry hydrogen, and the potassium sulphide remains stable at 560°. As $K_2S,5H_2O$ loses $5H_2O$, it is evidently not $KHS,KHO,4H_2O$. Sodium sulphide was obtained as $Na_2S,9H_2O$.

By saturation of a solution of potassium hydroxide with hydrogen sulphide, crystals of the composition $2KHS,H_2O$ were obtained, which, like the hydrates of the normal sulphide, could be dehydrated without loss of sulphur. The hydrosulphide was quite stable at 560°.

According to Sabatier, the hydrated crystals of sodium sulphide are easily converted into sodium hydrosulphide by the action of hydrogen sulphide, but the author shows that solutions of sodium sulphide will only take up sufficient hydrogen sulphide to form the hydrosulphide under certain rather restricted conditions as to concentration and temperature. Under favourable conditions, two hydrates were obtained, $NaHS,2H_2O$, $NaHS,3H_2O$, the latter being the stable form.

To prepare the polysulphides, sulphur was dissolved in gently heated solutions of the hydrosulphides, when the following potassium compounds were obtained: $K_4S_5,10H_2O$, $K_4S_5,6H_2O$, $K_4S_5,19H_2O$, K_4S_9,xH_2O, K_4S_{10},xH_2O, as well as substances approximating in composition to K_4S_8 and K_4S_7.

The only sodium compound obtained in this way was $Na_4S_5,14H_2O$.

*77. "On the relative efficiency of various forms of still-head for fractional distillation." By Sydney Young, D.Sc., F.R.S.

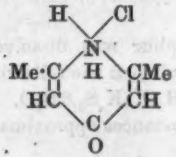
Experiments have been made to test the efficiency of the following forms of still-head, most of which are in general use: (1) plain vertical tubes of different lengths and widths; (2) sloping and spiral tubes; (3) vertical tube with bulbs (Wurtz); (4) the Hempel still-head; (5) the Glinsky dephlegmator; (6) the Le Bel-Henninger dephlegmator. In addition to these, a modified Young and Thomas dephlegmator and three new forms of still-head, descriptions of which are given in the paper, have been tested and compared with the others.

As the amount of liquid available for fractionation is often very limited, special attention has been paid to the suitability of the various forms of still-head for the distillation of small as well as of large quantities of liquid. Taking both efficiency and usefulness into account, it is shown that the new forms of still-head are superior to those in general use.

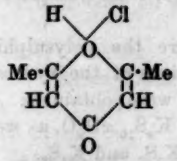
***78. "The salts of dimethylpyrone and the quadrivalence of oxygen." By J. N. Collie, Ph.D., F.R.S., and Thomas Tickle.**

The authors have investigated the series of salts formed by dimethylpyrone with acids. Dimethylpyrone forms, in aqueous solutions with various acids, crystallisable salts. The hydrochloride, hydrobromide, hydriodide, nitrate, oxalate, tartrate, chloracetate, salicylate, picrate, and platinochloride were prepared; these compounds are produced by direct addition of the acid to the dimethylpyrone without the elimination of water, as in the equation $C_7H_8O_2 + HCl = C_7H_8O_2HCl$. On solution in much water, they again break up into dimethylpyrone and the free acid.

Taking into account the molecular structure of dimethylpyrone, the method of preparation, and the properties of these compounds, the authors are inclined to believe that their constitution is similar to that of the salts of nitrogenous and other bases.



Dimethylpyridone chloride.



Dimethylpyrone chloride.

This, however, assumes that oxygen may behave as a quadrivalent element. In favour of this hypothesis, the authors instance such compounds as dimethyl ether hydrochloride, diethyl ether hydriodide, ether peroxide, &c., and they suggest that should compounds similar to the salts they have examined contain nitrogen, phosphorus, sulphur, or iodine, they could be regarded as derived from the hypothetical bases NH_4OH, PH_4OH, SH_3OH, IH_2OH respectively; hence dimethylpyrone may be looked upon as a derivative of OH_3OH or *oxonium hydrate*.

79. "The symmetrical di-isopropylsuccinic acids." By William A. Bone and C. H. G. Sprankling.

The authors have succeeded in preparing two isomeric symmetrical di-isopropylsuccinic acids, by the action of isopropyl bromide on the sodium derivative of ethyl isopropylcyansuccinate, and subsequent hydrolysis of the ethereal salt so obtained.

The *trans*-acid, which is quite insoluble in benzene, melts at 226° and has a dissociation constant $k = 0{\cdot}0108$. The *cis*-acid, which dissolves in warm benzene, melts at 171—172°, and has a dissociation constant $k = 0{\cdot}2255$. Both acids, on treatment with acetyl chloride, give their anhydrides, which are liquid. The anhydrides dissolve in sodium hydrate, forming the sodium salts of the original acids. The anhydride of the *trans*-acid, on being boiled with acetic anhydride for several hours, is converted into the *cis*-anhydride, so that, in this way, the *cis*-acid can be obtained from the *trans*-modification. The behaviour of the new acids with acetyl chloride and acetic anhydride is thus in all respects similar to that of the symmetrical dimethylsuccinic acids. The calcium salts of both acids are sparingly soluble.

Previous workers (Hell and Mayer, *Ber.*, 1889, **22**, 48; Auwers, *Ann.*, 1896, **292**, 162) have been able to obtain only the *cis*-acid. Auwers (*loc. cit.*) states that symmetrical di-isopropylsuccinic acid, unlike other symmetrical di-alkylsuccinic acids, exists only in one modification. The authors are also completing an investigation on the symmetrical dipropylsuccinic acids.

80. "Active and inactive phenylalkyloxyacetic acids." By Alex. McKenzie, M.A., D.Sc.

The replacement of the alcoholic hydrogen in active malic, lactic, and tartaric acids by alkyl groups causes a striking increase of optical activity. The primary object of the investigation was to ascertain the effect of a similar replacement in the much more highly active mandelic acid.

For the preparation of the active alkylated mandelic acids, the method of alkylation recently applied by Purdie and Pitkeathly (*Trans.*, 1899, **75**, 157) was adopted. Preliminary experiments with inactive mandelic esters showed that phenylalkyloxyacetic esters were produced. It was found convenient to start with free mandelic acid instead of its esters; thus, by the action of silver oxide and alkyl iodide on *i*-mandelic acid, phenylalkyloxyacetic acids were obtained.

By the interaction of silver oxide, ethyl iodide, and *l*-mandelic acid, a mixture of ethyl *l*-mandelate and *l*-phenylethoxyacetate results. After hydrolysis, *l*-phenylethoxyacetic acid was completely separated from mandelic acid as an oil. Polarimetric observations were made on the acid and on its sodium and barium salts.

l-Phenylmethoxyacetic acid is crystalline, m. p. 63—64°. The sparing solubility of its sodium salt in water afforded a ready method of separating it from mandelic acid. Rotations of the acid in various solvents and of several of its salts in water were made.

From *l*-mandelic acid, phenylpropyloxyacetic acid was obtained as an inactive oil; phenylisopropyloxyacetic acid was crystalline and active.

The molecular rotations of *l*-phenylmethoxyacetic acid and its salts are slightly higher than those of *l*-mandelic acid for equivalent concentrations. The rotations fall on dilution, a minimum being reached with the easily-dissociated salts, but with the acid, which in about 1/50 normal solution is 18 per cent. dissociated, the minimum had not been reached. Rimbach's results with *d*-mandelic acid (*Zeit. physikal. Chem.*, 1899, 28, 251) show similar relationships. The rotations for the ethoxy- and isopropyloxy-acids are considerably lower than those of *l*-mandelic acid.

Silver oxide has been used as an alkylating agent with tartrates and lactates without any observations of racemisation in the active products. Although every precaution was taken to avoid racemisation, so far, at least, as this is caused by violent action and rise of temperature, the propyloxy-acid was obtained inactive. Partial racemisation had also taken place in the preparation of ethyl *l*-phenylethoxyacetate by the silver salt method.

81. "The chemical composition of the oleo-resin of Dacryodes Hexandra." By A. More.

The oleo-resin consists of essential oil, a resin, and a white crystalline substance, $C_{25}H_{44}O$, melting at 166—167°.

The essential oil contains *lævorotatory pinene* and *lævorotatory sylvestrene*, which is the optical isomer of the sylvestrene described by Atterberg.

The crystalline substance is insoluble in water, and only sparingly soluble in strong alcohol. By the action of acetic anhydride, it yields a crystalline mono-acetate, m. p. 200°, and it therefore appears to be an alcohol. It is unaffected by potash and by all ordinary reagents. A tetranitro-derivative is produced by the action of fuming nitric acid. Chromic acid in acetic acid solution, while oxidising it, appears to cause two molecules to combine; the product is a feeble acid, the

molecular weight of which was determined by the cryoscopic method. The substance is probably identical with Personne's ilicic alcohol, m. p. 175°, with which it agrees in composition, and which gives an acetyl derivative melting at 204—206°.

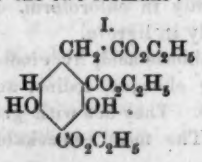
82. "The condensation of ethyl acetonedicarboxylate: the constitution of triethyl orcintricarboxylate." By David Smiles Jerdan.

In the first part of this paper, the author discusses the action of condensing agents on ethyl acetonedicarboxylate. Two condensation agents have already been described, namely, a triethyl orcintricarboxylate, $C_{16}H_{20}O_8$ (Cornelius and von Pechmann, *Ber.*, 1886, 19, 1446; von Pechmann and Wolman, *Ber.*, 1898, 31, 2014), and a lactone, $C_{12}H_{10}O_7$, which was discovered by the author (*Trans.*, 1887, 71, 1106), and shown to be a derivative of phloroglucinol. Triethyl orcintricarboxylate was originally obtained by the action of sodium on ethyl acetonedicarboxylate, and afterwards by dissolving the ester in alcohol, saturating the solution with hydrogen chloride, and allowing the mixture to stand some weeks. The lactone, $C_{12}H_{10}O_7$, was first prepared by the action of sodium on ethyl acetonedicarboxylate dissolved in benzene. The author has recently found that both substances are formed by the action of sodium ethylate on an alcoholic solution of ethyl acetonedicarboxylate, and further, that small quantities of a number of metals and of their oxides are capable of bringing about the condensation of relatively large quantities of ethyl acetonedicarboxylate. Thus the ester, when heated with one-eight-hundredth part of its weight of sodium, gives a 30 per cent. yield of triethyl orcintricarboxylate. The probable course of this reaction is discussed.

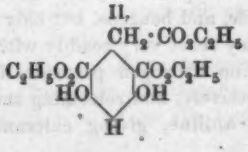
A new condensation product, $C_{14}H_{16}O_8$, which melts at 141°, has been obtained by the action of magnesium on ethyl acetonedicarboxylate in presence of ethyl chloracetate, and has been shown to be a *diethyl orcintricarboxylate*. It is derived from the same orcintricarboxylic acid as the triethyl ester already mentioned, as is proved by its conversion into the triethyl ester by esterification.

The second part of the paper contains the results of an investigation into the constitution of triethyl orcintricarboxylate. Cornelius and von Pechmann (*loc. cit.*) pointed out that this substance may have one or other of the two formulæ:

I.



II.



The author has obtained from triethyl orcintricarboxylate, and from the diethyl orcintricarboxylate (m. p. 141°) already mentioned, derivatives of two orcindicarboxylic acids, both of which have been shown to contain the group $-CH_2-COOH$. Only formula I, the asymmetric formula for triethyl orcintricarboxylate, admits of the formation of two such acids, namely:—

and accordingly this formula alone can correctly represent the constitution of triethyl orcintricarboxylate.

83. "A series of substituted nitrogen chlorides." By F. D. Chattaway and K. J. P. Orton.

Compounds in which halogen is attached to nitrogen have been little studied, although a number of isolated examples are known. In continuation of our work on nitrogen iodide, we have studied this nitrogen halogen linkage, and have obtained a very large number of compounds in which it occurs.

In this paper, the disubstitution products of nitrogen chloride are considered, containing formyl, acetyl, and benzoyl, together with a phenyl or a substituted phenyl residue.

These form a well-defined group of compounds, phenyl acetyl nitrogen chloride discovered by Bender being one of the simplest members.

They are readily obtained from the corresponding formanilide, acetanilide, or benzanilide by the action of hypochlorous acid under regulated conditions.

$$\begin{matrix}RCO\\R'\end{matrix}\!\!>\!NH + HOCl = \begin{matrix}RCO\\R'\end{matrix}\!\!>\!NCl + H_2O.$$

The method generally employed is to add gradually the calculated quantity of calcium hypochlorite to the anilide suspended in a saturated solution of potassium bicarbonate.

The substituted nitrogen chlorides are all stable solids of low melting point, crystallising well in large, colourless, transparent plates or prisms. They dissolve readily in chloroform, carbon bisulpide, and benzene, but only sparingly in ligroin.

They react very readily with hydrochloric acid, hydriodic acid, and alkaline hydrogen peroxide, liberating chlorine, iodine, and oxygen respectively, and reforming the anilide. They act with great energy upon aniline, giving chloranilines. The most remarkable change,

however, which these compounds undergo takes place when they are heated. When an unsubstituted phenyl group is attached to the nitrogen, the chlorine and the para-hydrogen atom of the nucleus change places, and a para-chloranilide is formed. With a para-chlorphenyl group attached to the nitrogen, a similar change takes place on heating, the chlorine, however, now going into the ortho-position. Similar changes are brought about when these nitrogen chlorides are warmed with water or dilute acids.

If, however, both the para- and ortho-positions in the phenyl nucleus are occupied, *e.g.*, by chlorine atoms, no intramolecular change ensues, but the molecule breaks down in a somewhat complicated way which apparently depends on the nature of the acid radicle attached to the nitrogen; in the case of the formyl and acetyl derivatives, chlorine is set free; with the benzoyl compound, benzoyl chloride is evolved. Phenyl acetyl nitrogen chloride has been prepared by the bicarbonate method, a theoretical yield being obtained; it crystallises in large, transparent plates.

The following compounds have been prepared:—

Phenyl formyl nitrogen chloride, $HCON(C_6H_5)\cdot Cl$, long, transparent prisms. M. p. 47°. *Para-chlor-phenyl formyl nitrogen chloride*, $HCON(C_6H_4Cl)\cdot Cl$, long, transparent prisms. M. p. 95—96°. 2 : 4-*dichlor-phenyl formyl nitrogen chloride*, $HCON(C_6H_3Cl_2)\cdot Cl$, colourless, transparent plates. M. p. 44°. *Para-chlor-phenyl acetyl nitrogen chloride*, $CH_3CON(C_6H_4Cl)\cdot Cl$, colourless plates. M. p. 82°. 2 : 4 *dichlor-phenyl acetyl nitrogen chloride*, $CH_3CON(C_6H_3Cl_2)\cdot Cl$, large, glittering plates. M. p. 68°. *Phenyl benzoyl nitrogen chloride*, $C_6H_5CON(C_6H_5)\cdot Cl$, colourless plates. M. p. 77°. 2 : 4-*dichlor-benzoyl nitrogen chloride*, $C_6H_5CON(C_6H_3Cl_2)\cdot Cl$, large, colourless plates. M. p. 86°.

We believe that the oil obtained by Witt, and regarded by him as a hypochlorous acid addition product of 2 : 4-dichlor-acetanilide, is impure 2 : 4-dichlor-phenyl acetyl nitrogen chloride.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Berthelot, M. Chimie végétale et agricole. (Station de chimie végétale de Meudon, 1883—1899.) 4 vols. Paris. 1899. From the Author.

Clowes, F. A Treatise on Practical Chemistry and Qualitative Analysis. Seventh edition. London. 1899. From the Author.

Furnival, W. J Researches on Leadless Glazes. Stone. 1899. From the Author.

Murrill, P. I. Alkaloidal Estimation. A Bibliographical Index of Chemical Research prepared from original literature for the Committee of Revision. (Committee of Revision and Publication of the Pharmacopœia of the United States of America, 1890—1900.) Ann Arbor. 1898. From the Editor.

Richter, V. von. Edited by R. Anschütz. Organic Chemistry. Vol. I. Chemistry of the Aliphatic Series. Translated by E. F. Smith. Third American from eighth German edition. London. 1899. From the Publishers.

II. *By Purchase.*

Dupont, J., et Freundler, P. Manual opératoire de chimie organique. Paris. 1898.

Jörgensen, A. Les Microorganismes de la Fermentation. Traduit par P. Freund, et revisé par l'auteur. Deuxième edition française. Paris. 1899.

Kayser, E. Die Hefe. Morphologie und Physiologie: praktische Bedeutung der Hefereinzucht. Ausgabe von E. P. Meinecke. München. 1898.

Silbermann, H. Die Seide; ihre Geschichte, Gewinnung, und Verarbeitung. 2 vols. Dresden. 1897.

Thomson, J. J. The Discharge of Electricity through Gases. London. 1898.

Traube, J. Physico-Chemical Methods: Translated by W. L. Hardin. Philadelphia. 1898.

At the next meeting, on Thursday, June 15th, there will be a ballot for the election of Fellows, and the following papers will be communicated by the authors:—

"On the decomposition of chlorates, with special reference to the evolution of chlorine and oxygen." By W. H. Sodeau, B.Sc.

"The action of hydrogen peroxide on formaldehyde." By A. Harden, M.Sc., Ph.D.

"Homocamphoronic and camphononic acids." By A. Lapworth and E. M. Chapman.

"Action of silver compounds on α-dibromocamphor." By A. Lapworth.

"The colouring matter of cotton flowers." By A. G. Perkin.

"Experiments on the synthesis of camphoric acid." By H. A. Auden, W. H. Perkin, jun., and J. L. Rose.

"Methylisoamylsuccinic acid. Part I." By W. T. Lawrence.

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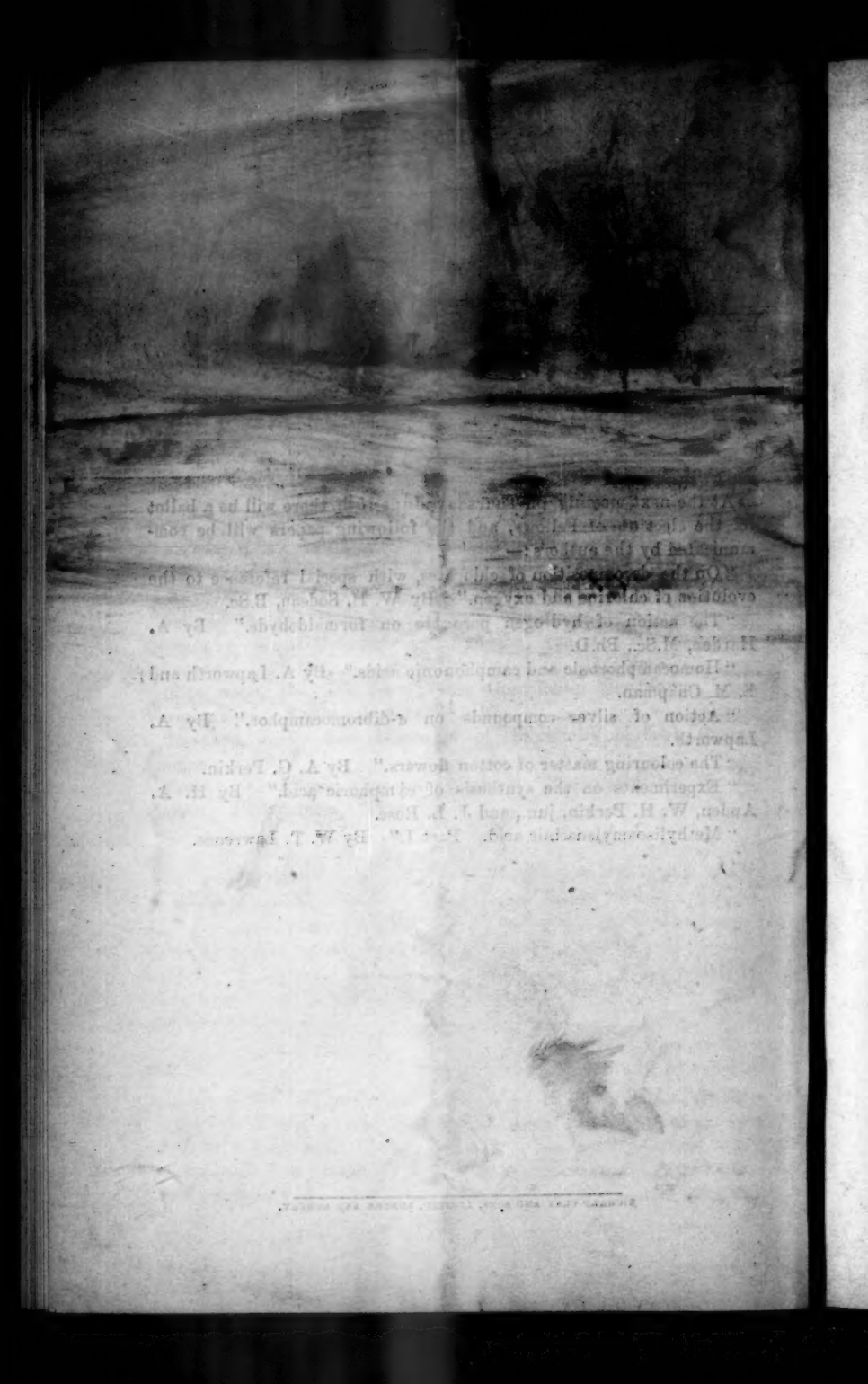


Issued 24/6/1899

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 15. No. 212.

June 15th, 1899. Professor T. E. Thorpe, F.R.S., President, in the Chair.

Messrs. A. R. Foulerton, S. B. Schryver, and J. P. de Castro were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Percy Kay, 3, Phene Street, Chelsea, S.W.; Hugh Main, 45, The Vicarage, Old Charlton, Kent.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Robert Henry Aders, George Dekeyne Atkinson, Percy Bean, Walter Lionel Blackman, Wilfred Carpmael, James Connah, B.Sc., Henry Meldola Danziger, Frederick Doyle, Frederick Charles Dunscombe, William Frederick Eichenauer, F. N. Ashcroft Fleischmann, William Gordon Fraser, Frederick Hutton Getman, Julius Hübner, Edward Charles Johnson, Arthur Alexander Leon, James McAlley, Robert McClumpha, George Alfred Parkes, Stanley John Peachey, Eskricke Sidney Phillips, B.A., Sidney Rossiter, Henry Royal-Dawson, William F. John Shepheard, John William Shepherd, B.Sc., Charles Simmonds, B.Sc., John Ward Stainer, Samuel Stansfield, B.Sc., George Hardstaff West, B.Sc., Christopher Joseph Whittaker.

Of the following papers, those marked * were read:—

*84. "On the decomposition of chlorates, with special reference to the evolution of chlorine and oxygen." By W. H. Sodeau, B.Sc.

Some chlorates, on being heated, give off almost all their chlorine as such, whilst other chlorates give none. According to Schulze,

the chlorate breaks up into chloride and oxygen, the chlorine evolved being due to the nascent oxygen attacking the chloride, whilst Spring and Prost regard the chlorate as decomposing into oxide, chlorine, and oxygen, the chlorine being more or less reabsorbed. The author points out that in addition to these two theories two others are possible, (1) that chlorates may break up in both of these ways simultaneously, and (2) that chloride and oxide may represent the balanced action of chlorine and oxygen.

His experiments have been made chiefly with potassium and barium chlorates. The former gives no chlorine, whether the pressure of the evolved gas be kept at 1 mm. or at 1 atmosphere. With barium chlorate, however, 0·066 per cent. of the total chlorine was evolved when the pressure was kept at 1 to 2 mm. and the duration of the experiment 233 minutes, whilst at atmospheric pressure, 0·093 was obtained when the duration was 165 minutes, but when very rapidly decomposed (half a minute), the percentage of chlorine evolved rose to 0·705. These are the averages of several experiments.

From the results of his experiments, the author concluded that when barium chlorate is heated, it undergoes two decompositions at the same time: (*a*) an exothermic decomposition into chloride and oxygen, (*b*) an endothermic decomposition into oxide, chlorine, and oxygen, and that no appreciable reaction takes place between the chloride and oxygen (or chlorate), or between the oxide and chlorine, but that the increase of chlorine in a rapid decomposition may be ascribed to the great rise of temperature favouring the endothermic reaction. He believed that potassium chlorate decomposed directly into chloride and oxygen. Further experiments were being conducted on the behaviour of manganese oxides with potassium chlorate, and on the decomposition of pure lead and calcium chlorates. The experiments already performed with these chlorates appeared to confirm the author's view that these two independent reactions occurred.

***85. "Action of hydrogen peroxide on formaldehyde." By A. Harden, M.Sc., Ph.D.**

When solutions of hydrogen peroxide and formaldehyde are mixed, no reaction appears to take place, but when the liquid is made strongly alkaline with soda, hydrogen is evolved. The reaction occurs according to the equation $H_2O_2 + 2CH_2O + 2NaOH = 2H{\cdot}CO_2Na + H_2 + 2H_2O$. Hydrogen peroxide, therefore, when treated with alkaline formaldehyde, gives a volume of hydrogen exactly equal to the volume of oxygen which it would give with potassium permanganate and sulphuric acid.

The reaction proceeds slowly and incompletely unless a large excess

of alkali be present. When hydrogen peroxide is treated with excess of formaldehyde, the reaction takes place rapidly and completely, and the hydrogen which is evolved is pure. When, on the other hand, formaldehyde is treated with excess of hydrogen peroxide, the reaction is incomplete and proceeds very slowly, whilst the gas evolved contains oxygen. Hence the reaction does not appear adapted for the quantitative estimation of formaldehyde in aqueous solutions.

Cuprous oxide and soda give a somewhat similar reaction with formaldehyde. This reaction was described by Loew (*Ber.*, 1887, 20, 145) as a catalytic reaction, but it appears in reality to be a quantitative one, expressed by the equation $Cu_2O + 2NaOH + 2CH_2O = Cu_2 + H_2 + 2H{\cdot}CO_2Na + H_2O$. Cupric oxide also gives a similar reaction, two atoms of hydrogen being liberated for each atom of oxygen in the oxide.

When caustic soda and then formaldehyde are added to a solution of copper sulphate and the liquid gently warmed, the cupric hydroxide is reduced to cuprous oxide without evolution of hydrogen, and when the temperature is subsequently raised, the cuprous oxide reacts as described above. When, on the other hand, caustic soda is added to a boiling solution of copper sulphate, the liquid cooled, and formaldehyde then added, no reduction to cuprous oxide occurs on warming, but metallic copper is formed, and twice as much hydrogen is evolved as in the previous case.

Manganese dioxide does not appear to be reduced by formaldehyde, whilst the oxides of mercury and bismuth are reduced without evolution of hydrogen.

Discussion.

Mr. Cross said that he regarded the author's results as additional evidence that hydrogen peroxide tends to react as H_2O_2, as it was clear that, in this case, it could not react as H_2O,O.

Dr. Debus pointed out that, in acting as an oxidising agent, hydrogen peroxide usually broke up into water and oxygen, but since aldehydes in many reactions behave as hydrides, we might suppose that the equation $2H{\cdot}CHO + (HO)_2 = 2(HO{\cdot}CHO) + H_2$ represented the change, the hydrogen set free coming from the aldehyde.

*86. "Homocamphoronic and camphononic acids." By Arthur Lapworth and Edgar M. Chapman.

α-Dibromocamphor, though scarcely affected by the ordinary mild oxidising agents, is rapidly attacked by dilute nitric acid in presence of silver nitrate. The greater portion of the substance is reduced to monobromocamphor and camphor, but a small quantity is converted into a neutral *nitro*-compound, $C_{10}H_{14}N_2O_6$, which crystallises in beautiful,

orthorhombic prisms melting at 93—94°. A still smaller quantity of the dibromo-compound is converted into an *acid*, $C_{10}H_{16}O_6$, which is found to be identical with the substance obtained by Forster (*Trans.*, 1896, 69, 49) on oxidising bromocamphoronic acid with dilute permanganate. The authors find that this acid is tribasic, and for it they propose the name *homocamphoronic acid*; it is an open chain tricarboxylic acid, and its constitution must be represented by one of two formulæ, $CO_2H\cdot CMe_2\cdot CMe(CO_2H)\cdot CH_2\cdot CH_2\cdot CO_2H$ or $CO_2H\cdot CH_2\cdot CMe_2\cdot CMe(CO_2H)\cdot CH_2\cdot CO_2H$, of which the former seems to be the more probable. Homocamphoronic acid is optically active; in 2 per cent. aqueous solution $[\alpha]_D = -34{\cdot}96°$. It is somewhat sparingly soluble in water, and separates from aqueous solution in small prisms which give off water and melt, according to the rate of heating, between 180° and 208°, the latter temperature being probably the true melting point. *Anhydrohomocamphoronic acid*, $CO_2H\cdot C_7H_{13}\begin{matrix}CO\\CO\end{matrix}>O$, is made by heating the acid or by warming it with acetyl chloride; it crystallises in prisms melting at 86—87°. The aniline derivative, $(CO_2H)_2\cdot C_7H_{13}CO\cdot NHPh$, melts at 98—100°, and the paratoluidine derivative, $(CO_2H)_2\cdot C_7H_{13}\cdot CO\cdot NH\cdot C_7H_7$, at 163—164°.

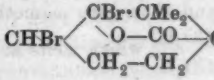
When anhydrohomocamphoronic acid is heated to 200—260°, it loses carbon dioxide and yields an acid having the formula $C_9H_{14}O_3$. This substance is a saturated cyclic ketonic acid having the structure $\begin{matrix}CO\cdot CMe_2\\|\\CH_2\cdot CH_2\end{matrix}>CMe\cdot CO_2H$ or $\begin{matrix}CH_2\cdot CMe_2\\|\\CO\text{—}CH_2\end{matrix}>CMe\cdot CO_2H$, and, therefore, containing the carbon atoms in the position assumed by Bredt and Perkin for nine of the ten atoms in camphoric acid. The substance is, in fact, identical with a ketonic acid obtained by J. Walker as a bye-product in the electrolysis of ethyl allocamphorate. Dr. Walker was good enough to send the authors a small specimen of his acid for comparison, and the identity of the two substances has been completely established; he has, moreover, agreed to the name *camphononic acid*, which the authors propose for it. It melts at 228°, and has all the properties assigned to it by Walker. The phenylhydrazone, $CO_2H\cdot C_8H_{13}{:}N\cdot NHPh$, crystallises in colourless needles melting at 174°. The *bromophenylhydrazone*, $C_{15}H_{19}O_2N_2Br$, forms transparent prisms and melts at 194—195°. The *semicarbazone* crystallises in needles and melts and decomposes at 230—232°.

When camphononic acid is very carefully oxidised with dilute nitric acid, a large quantity of camphoronic acid, which is apparently the sole product, is obtained.

***87. "Action of silver compounds on α-dibromocamphor." By Arthur Lapworth.**

The formation of homocamphoronic acid from α-dibromocamphor by the action of dilute nitric acid and silver nitrate is preceded by the production of an unsaturated acid, $C_{10}H_{15}BrO_2$, identical with bromocamphorenic acid, which was first obtained by the reduction of α-dibromocampholid (Forster, *Trans.*, 1896, **69**, 46). This substance may be obtained by heating a solution of α-dibromocamphor in acetic acid or alcohol with silver nitrate, acetate, or oxide; the amount formed is small, however (10—20 per cent.), the greater portion of the dibromocamphor undergoing reduction.

The formation of bromocamphorenic acid appears at first to be due to hydrolysis, represented empirically by the equation $C_{10}H_{14}Br_2O + H_2O = C_{10}H_{15}BrO_2 + HBr$. As bromocamphorenic acid at once loses hydrogen bromide when treated with cold dilute potassium permanganate, and is subsequently converted into homocamphoronic acid, it seems certain that it contains the group –CH=CBr– as a part of the closed chain; and as dibromocamphor contains the group $-CBr_2 \cdot CO-$, it would appear that, in the formation of bromocamphorenic acid, these two carbon atoms are separated, and that one of them enters the second pentamethylene ring. Of the possible formulæ for bromocamphorenic acid, which are, of course, easily derived from the two possible formulæ for homocamphoronic acid (see preceding note) the formula $CH\langle^{CBr \cdot CMe_2}_{CH_2 \cdot CH_2}\rangle CMe \cdot CO_2H$ is the one which is most in accordance with the facts which have been observed, the corresponding formula for dibromocampholid being



88. "The colouring matter of cotton flowers." By A. G. Perkin.

The flowers of the cotton plant, *Gossypium herbaceum*, are employed as a dyestuff in the Manipur district of India. They contain as glucoside a new colouring matter, *gossypetin*, $C_{16}H_{12}O_8$, soluble in alkalis with an orange-red colour, becoming green on oxidation. The *hexacetyl* compound, $C_{16}H_6O_8Ac_6$, colourless needles, m. p. 212—216°; the *sulphate*, $C_{16}H_{12}O_8,H_2SO_4$, the *hydriodide*, $C_{16}H_{12}O_8,HI$, orange-red needles, and the *monopotassium* salt, $C_{16}H_{11}O_8K$, a crystalline powder, have been prepared. Gossypetin contains no methoxyl groups, and on fusion with alkali yields phloroglucinol and protocatechuic acid. It is probably a member of the flavone group of colouring matters. Gossypetin is similar to, but not identical with, thujetin, which is present in *Thuja occidentalis* (Kawalier, *Jahresbericht*, 1858, 512).

Note on Rottlerine.—The decomposition products of rottlerine, $C_{33}H_{30}O_9$, a colouring matter of kamala, *Mallotus Phillipinensis*, previously described (*Trans.*, 1893, **65**, 981; 1895, **67**, 230), are with fused alkali acetic and benzoic acids, and with nitric acid *o*- and *p*-nitrocinnamic acids. It has now been found that fused alkali at 220—240° yields also phloroglucinol.

89. "Experiments on the synthesis of camphoric acid." By H. A. Auden, W. H. Perkin, jun., and J. L. Rose.

These experiments were instituted with the object of preparing an acid of the formula $\begin{matrix} CO_2H\cdot \overset{*}{C}OH\cdot Me & HC(Me)_2 \\ CO_2H\cdot CH-CH_2- & -CH_2 \end{matrix}$, in the hope that it might prove possible to eliminate water between the points marked *, and thus obtain an acid, $\begin{matrix} CO_2H\cdot C(Me)- & -C(Me)_2 \\ CO_2H\cdot CH\cdot CH_2\cdot & CH_2 \end{matrix}$, which would have the constitution first suggested by Perkin (*Proc.*, 1896, **12**, 191) as a possible expression of the constitution of camphoric acid. Ethyl isoamylacetoacetate was dissolved in ether and treated at a low temperature with potassium cyanide and hydrochloric acid, when ethyl *a*-isoamyl-$\beta\beta$-hydroxycyanobutyrate, $Me(CN)C(OH)\cdot CH(C_5H_{11})\cdot CO_2Et$, was obtained as a thick oil, which, on hydrolysis with alcohol and hydrochloric acid, yielded as principal product methylhydroxyisoamylsuccinimide, $\begin{matrix} Me\cdot C(OH)\cdot CO \\ C_5H_{11}\cdot CH-CO \end{matrix}>NH$ (m. p. 104°.)

This substance, when boiled with sodium carbonate, is first converted into the corresponding amide, which crystallises from water and melts at 183°, and then into *aa*-methylhydroxy-*a'*-isoamylsuccinic acid, $\begin{matrix} Me\cdot C(OH)\cdot CO_2H \\ C_5H_{11}\cdot CH-CO_2H \end{matrix}$, which melts at 66°, and yields a silver salt of the formula $C_{10}H_{16}O_5Ag_2$. As this acid has the constitution represented by the formula given at the commencement of this abstract, experiments were next made with the object of eliminating water in such a way as to obtain a saturated acid of the same composition as camphoric acid, but without success. When the acid is subjected to distillation, water is eliminated and an oil, distilling at 260°, is obtained, which, after careful investigation, has been found to be methylisoamylmaleic anhydride, $\begin{matrix} Me\cdot C\cdot CO \\ C_5H_{11}\cdot C\cdot CO \end{matrix}>O$. This anhydride dissolves in potash solution, but on acidifying, the anhydride, and not the acid, separates, a behaviour which is exactly similar to the case of xeronic acid, $\begin{matrix} Et\cdot C\cdot CO_2H \\ Et\cdot C\cdot CO_2H \end{matrix}$, which, when set free from its salts, is obtained in the form of its anhydride.

The solution of methylisoamylmaleic anhydride in benzene gives, with aniline, the anil $C_{16}H_{19}O_2N$, which crystallises from methyl alcohol and melts at 70°. When the anhydride is reduced with hydriodic acid and phosphorus, it yields a mixture of *cis*- and *trans*-methylisoamylsuccinic acids, $\begin{matrix} Me—CH\cdot CO_2H \\ | \\ C_5H_{11}\cdot CH\cdot CO_2H \end{matrix}$, the former of which melts at 92° and the latter at 142° (see following abstract).

Ethyl isoamylacetoacetate is readily reduced by sodium amalgam, forming α-isoamyl-β-hydroxybutyric acid, $Me\cdot CHOH\cdot CH(C_5H_{11})\cdot CO_2Et$, a thick oil, which, on distillation, decomposes with elimination of water and formation of α-isoamylcrotonic acid, $Me\cdot CH{:}C(C_5H_{11})\cdot CO_2H$ (b. p. 240°). That ring-formation had not taken place in this case was shown by the fact that the acid obtained is unsaturated, and, on oxidation, yields isobutylacetic acid, $C_5H_{11}CO_2H$. When isoamylacetone, $C_5H_{11}\cdot CH_2\cdot CO\cdot Me$, is treated with hydrocyanic acid and the product hydrolysed, a small quantity of α-hydroxy-β-isoamylisobutyric acid, $C_5H_{11}\cdot CH_2\cdot C(OH)(Me)\cdot CO_2H$, is formed, which melts at 66°, and is isomeric with the isoamylhydroxybutyric acid mentioned above.

90. "Methylisoamylsuccinic acid. I." By W. Trevor Lawrence.

The author is preparing methylisoamylsuccinic acid in large quantities, in order to obtain from it, if possible, by oxidation or bromination and subsequent splitting off of water or hydrogen bromide respectively, an acid possessing the constitution of camphoric acid (see preceding abstract) suggested by Perkin in 1896, and independently in 1897 by Bouveault (*Bull. Soc. Chim.*, iii, 17, 990); this paper contains only such results as confirm those of Auden, Perkin, and Rose.

When ethyl α-methyl-α′-cyansuccinate, isoamylbromide, and sodium ethylate are heated, in molecular proportions, and the product of the condensation distilled under diminished pressure, ethyl α-methyl-α′-cyan-α′-isoamylsuccinate, $CO_2EtC(C_5H_{11})(CN)\cdot CH(Me)CO_2Et$, is obtained (b. p. 182°, 30 mm.), which, on hydrolysis with alcoholic potash, gives after acidifying, a semi-solid acid mass, probably consisting of the cyansuccinic acid. A similar acid was also prepared as follows:

Isoamylacetic acid is converted by bromine and phosphorus pentabromide into the acid bromide of α-bromisoamylacetic acid, which, with alcohol, gives ethyl α-bromisoamylacetate, $C_5H_{11}CHBr(CO_2Et)$, (b. p. 146°, 65 mm.); this condenses with ethyl sodiocyanacetate to form ethyl α-cyan-α′-isoamylsuccinate (b. p. 196°, 35 mm.).

Ethyl α-cyan-α′-isoamylsuccinate, $CO_2Et\cdot CH(CN)\cdot CH(C_5H_{11})(CO_2Et)$, is converted into isoamylsuccinic acid, $(CO_2H)\cdot CH_2\cdot CH(C_5H_{11})CO_2H$,

(m. p. 76°), on hydrolysis, and is identical with the acid obtained by Fittig and Schirmacher (*Annalen*, 1898, **304**, 295)—on treatment with methyl iodide and sodium ethylate, it is converted into ethyl α-cyan-α-methyl-α′-isoamylsuccinate, $CO_2Et\cdot C(CN)(Me)\cdot CH(C_5H_{11})CO_2Et$, (b. p. 185°, 30 mm.), which, on hydrolysis, gives a similar cyansuccinic acid to the one mentioned above.

Both of these cyan-acids give, on hydrolysis, a mixture of *trans*- and *cis*-methylisoamylsuccinic acids, $CO_2H\cdot CH(Me)\cdot CH(C_5H_{11})(CO_2H)$, which may be separated either by distillation in a current of steam, in which the *cis*-acid is volatile, or by means of ligroin, in which the *trans*-acid is insoluble.

trans-Methylisoamylsuccinic acid crystallises from benzene or hot water in prisms (m. p. 141—142°), and is converted by acetyl chloride into the anhydride (b. p. 170°, 25 mm.).

cis-Methylisoamylsuccinic acid is not easily recrystallised; it is obtained from the pure anhydride as a crystalline powder (m. p. 93°); the anhydride is obtained as an oil (b. p. 187°, 50 mm.) by the action of acetyl chloride. The anil melts at 116°.

This anhydride, heated with bromine and chloroform in a sealed tube for ten hours, is converted into β-isoamylcitraconic anhydride, $C_5H_{11}C(CO)=C(Me)CO>O$, an oil (b. p. 170°, 50 mm.); the free acid does not appear to exist.

On treatment with aniline, the anhydride, which reduces permanganate in the cold, is converted into the characteristic anil, which crystallises from methyl alcohol in needles, (m. p. 71°).

91. "Condensations of anhydracetonebenzil and its analogues with aldehydes." By Francis R. Japp., F.R.S., and Alexander Findlay, M.A., B.Sc.

The authors find that anhydracetonebenzil (diphenylcyclopentenolone) and benzaldehyde interact in presence of alcoholic potash according to the equation

$$Ph\cdot C(=CH)\cdot Ph\cdot C(OH)\cdot CH_2>CO + Ph\cdot CHO = H_2O + Ph\cdot C(=CH)\cdot Ph\cdot C(OH)\cdot C(=CHPh)>CO$$

Benzylideneanhydracetonebenzil (m. p. 230°).

In like manner, by acting on anhydracetonebenzil with cuminaldehyde, they obtained *cumylideneanhydracetonebenzil*, $C_{27}H_{24}O_2$ (m. p. 148°); and with cinnamaldehyde, *cinnamylideneanhydracetonebenzil*, $C_{26}H_{20}O_2$ (m. p. 222°).

By reduction with hydriodic acid, benzylideneanhydracetonebenzil

yields a compound $C_{24}H_{18}O$ (m. p. 182°)—probably a *benzylidene-diphenylcyclopentenone*.

The authors have applied the interaction with benzaldehyde to determining the constitution of the monosubstitution derivatives of anhydracetonebenzil, in which there is a doubt as to whether the substitution occurs in the CH- or in the CH_2-group. The condensation cannot occur except in the case of derivatives containing the CH_2-group intact. Thus Japp and Lander assigned to the monalkyl derivatives the formula $\begin{matrix}Ph\cdot C\!=\!\!=\!\!=\!CH\\ Ph\cdot C(OH)\cdot CHR'\end{matrix}\!>\!CO$, and in accordance with this, it was found that amylanhydracetonebenzil does not interact with benzaldehyde. On the other hand, *a*-anhydrobenzil-lævulic (*a*-anhydracetonebenzilethyloic) acid, in accordance with the formula ascribed to it by Japp and Murray, gives *benzylidene-a-anhydro-benzillævulic acid*, $\begin{matrix}Ph\cdot C\!=\!\!=\!\!=\!C\!-\!CH_2\cdot CO_2H\\ \quad\quad\quad\

whilst boiling with *dilute* potash transforms the oxazolone into a salt of the acid.

When the acid is heated with *strong* potash, it parts with carbon dioxide, and yields *benzimidobenzhydrylic oxide*, $Ph\cdot C(NH)\cdot O\cdot CHPh_2$ (needles, m. p. 172—173°). The constitution of the latter compound was proved by its synthesis from benzonitrile and benzhydrol under the influence of gaseous hydrogen chloride. It thus belongs to the class of imido-ethers described by Pinner and Klein (*Ber.*, 1877, 10, 1889).

Both the oxazolone and the acid, when boiled for a few minutes with fuming hydriodic acid, yield benzamide and diphenylacetic acid. Under the same conditions, benzimidobenzhydrylic oxide gives diphenylmethane in place of diphenylacetic acid.

None of the other nitriles and α-hydroxy-acids with which the authors experimented yielded compounds corresponding with the foregoing.

93. "Interaction of phenanthraquinone, acetophenone, and ammonia." By Francis R. Japp, F.R.S., and Andrew N. Meldrum, B.Sc.

Japp and Streatfeild showed (*Trans.*, 1882, 41, 270) that phenanthraquinone, acetone, and ammonia interact according to the equation $C_{14}H_8O_2 + C_3H_6O + NH_3 = C_{17}H_{15}NO_2 + H_2O$, and to the compound thus formed the constitution $\begin{matrix} C_6H_4\cdot C(OH)\cdot CH_2\cdot Ac \\ C_6H_4\cdot C:NH \end{matrix}$ was assigned by Japp and Miller (*Trans.*, 1885, 47, 12). The results of the present investigation, however, render the constitution $\begin{matrix} C_6H_4\cdot C(NH_2)\cdot CH_2\cdot Ac \\ C_6H_4\cdot CO \end{matrix}$, analogous to that of diacetonamine, more probable. The compound may be named *acetonylaminophenanthrone*.

Thus the authors find that phenanthraquinone, acetophenone and alcoholic ammonia interact according to the equation $\begin{matrix} C_6H_4\cdot CO \\ C_6H_4\cdot CO \end{matrix} + 2CH_3\cdot CO\cdot Ph + 2NH_3 = \begin{matrix} C_6H_4\cdot C(NH_2)\cdot CH_2\cdot CO\cdot Ph \\ C_6H_4\cdot C(NH_2)\cdot CH_2\cdot CO\cdot Ph \end{matrix} + 2H_2O$, yielding *diphenacyldiaminodihydrophenanthrene*, which crystallises in colourless, silky needles, and decomposes about 150° without showing a definite melting point. It is evident that a constitution analogous to that ascribed by Japp and Miller to the acetone-ammonia derivative of phenanthraquinone is not possible in the case of this compound.

The acetophenone-ammonia derivative is hydrolysed by aqueous oxalic acid according to the equation $\begin{matrix} C_6H_4\cdot C(NH_2)\cdot CH_2\cdot CO\cdot Ph \\ C_6H_4\cdot C(NH_2)\cdot CH_2\cdot CO\cdot Ph \end{matrix} +$

$2H_2O = \begin{matrix} C_6H_4\cdot C(OH)\cdot CH_2\cdot CO\cdot Ph \\ | \\ C_6H_4\cdot CO \end{matrix} + CH_3\cdot CO\cdot Ph + 2NH_3$, yielding *phenacylhydroxyphenanthrone* (*acetophenonephenanthraquinone*), which crystallises in small prisms or six-sided plates melting, with decomposition, at 125—130°.

By the interaction of phenanthraquinone, acetophenone, and aqueous ammonia, *phenacylaminophenanthrone*, $\begin{matrix} C_6H_4\cdot C(NH_2)\cdot CH_2\cdot CO\cdot Ph \\ | \\ C_6H_4\cdot CO \end{matrix}$, analogous to the acetone-ammonia derivative, was obtained. It crystallises in minute, colourless, six-sided plates melting about 160° with decomposition and evolution of gas. A substance, apparently identical with the foregoing, was obtained by the action of ammonia on phenacylhydroxyphenanthrone.

The ease with which these compounds break up into their generating substances renders a detailed study of their constitution impossible.

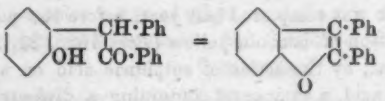
Other ketones, such as methyl ethyl ketone and diethyl ketone, appeared to interact in a similar manner with phenanthraquinone and ammonia; but it was found impossible to obtain the resulting compounds in a state of purity.

94. "Furfuran derivatives from benzoin and phenols." By Francis R. Japp, F.R.S., and Andrew N. Meldrum, B.Sc.

By the action of cold, concentrated sulphuric acid on a mixture of benzoin and phenol, Japp and Wadsworth (*Trans.*, 1890, **58**, 965) obtained paradesylphenolsulphonic acid, from which, by hydrolysing it with strong hydrochloric acid at 150°, paradesylphenol, $\begin{matrix} Ph\cdot CH\cdot C_6H_4\cdot OH \\ | \\ Ph\cdot CO \end{matrix}$ (1 : 4), was prepared.

The authors find that, by heating a mixture of benzoin and phenol with sulphuric acid of 73 per cent. strength, the foregoing condensation occurs without subsequent sulphonation of the resulting compound, and an excellent yield of paradesylphenol is obtained. The various condensations described in this note were effected by means of a sulphuric acid of this strength.

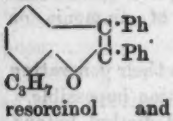
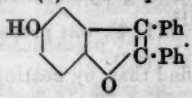
If the desyl-group were to take up the ortho-position towards the hydroxyl of the phenol, it is evident that, by a further elimination of water, a furfuran derivative might be formed:



$+ H_2O.$

With phenol and benzoin, no such reaction occurs; the para-compound alone is formed. With thymol and benzoin, however, a mixture

of desylthymol and cymodiphenylfurfuran is obtained. In the case of resorcinol and of quinol, either one or two diphenylfurfuran groups may be introduced. With phloroglucinol, only the compound containing three such groups was obtained.

The following compounds have been prepared: (1) From thymol and benzoin. *Desylthymol*, $\begin{matrix}Ph\cdot CH\cdot C_6H_2(Me)(C_3H_7)OH\\ |\\ Ph\cdot CO\end{matrix}$. Laminæ melting at 126°. The acetyl derivative forms needles melting at 110°. The position of the desyl group in desylthymol is uncertain, except that it is not adjacent to the hydroxyl group. *Cymodiphenylfurfuran*,  Slender needles melting at 115—116°. (2) From resorcinol and benzoin. *Metahydroxybenzodiphenylfurfuran*, $C_6H_3(OH)\langle\begin{matrix}CPh{:}C\cdot Ph\\ O\text{——}\end{matrix}\rangle$. Slender needles, with satiny lustre, melting at 117·5°. The acetyl derivative crystallises in slender prisms, melting at 117°. The practical coincidence in the melting points of these two substances is anomalous. They differ greatly in their other physical properties. *Metabenzotetraphenyldifurfuran*, $C_6H_2\left(\begin{matrix}CPh{:}C\cdot Ph\\ O\text{——}\end{matrix}\right)_2$. Slender needles, melting at 217—219°. Solutions show a violet fluorescence. Two constitutions, between which it is at present impossible to decide, might be assigned to each of these derivatives. Isomeric forms were not observed. (3) From quinol and benzoin. *Parahydroxybenzodiphenylfurfuran*,  Flat needles, melting at 158—160°. The acetyl derivative forms laminæ melting at 137°. *Parabenzotetraphenyldifurfuran*, $C_{34}H_{22}O_2$. Constitution analogous to that of the corresponding resorcinol derivative. Only one of the two possible isomerides observed. Needles melting at 278°. Solutions strongly fluorescent; crystals slightly so. (4) From phloroglucinol and benzoin. *Benzohexaphenyltrifurfuran*, $C_6\left(\begin{matrix}CPh{:}C\cdot Ph\\ O\text{——}\end{matrix}\right)_3$. Slender needles, melting at 360°.

The foregoing work was completed last year, before the publication of Graebe's investigation of benzoin yellow (*Ber.*, 1898, 31, 2975), in which it is shown that, by the action of sulphuric acid on a mixture of benzoin and gallic acid, a compound containing a diphenylfurfuran group is formed.

95. "Interaction of benzoin with phenylenediamines." By Francis R. Japp, F.R.S., and Andrew N. Meldrum, B.Sc.

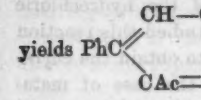
By heating benzoin with aniline and a little aniline hydrochloride, Japp and Murray (*Trans.*, 1894, **65**, 892) obtained 2′:3′-diphenylindole. The desylanilide, Ph·CO·CH(NH·Ph)·Ph, which is formed in the first instance, parts with water, under the influence of the hydrochloric acid, yielding the indole. The authors have now studied this reaction with the phenylenediamines, in order, if possible, to obtain the corresponding benzodipyrrhole derivatives. Only in the case of metaphenylenediamine, however, did the reaction take place in the desired sense.

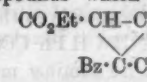
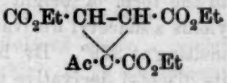
Benzoin, heated with metaphenylenediamine and a little of its hydrochloride, gave *metabenzotetraphenyldipyrrhole*, $C_6H_2\left(\begin{matrix}CPh{:}C\cdot Ph\\ NH\text{—}\end{matrix}\right)_2$, which forms slender needles melting at 282°. Two constitutions are possible for this compound, and at present there is apparently no means of deciding between them. Substituting paraphenylenediamine and its hydrochloride for the meta-compounds in the foregoing reaction, *bidesylparaphenylenediamine*, $C_6H_4(NH\cdot CH\,Ph\cdot CO\cdot Ph)_2$, was obtained in the form of bright yellow, minute laminæ melting at 257°. It yields a diacetyl derivative crystallising in slender, colourless needles melting at 279°. By heating either bidesylparaphenylenediamine or its diacetyl derivative with zinc chloride, or by heating benzoin with paraphenylenediamine hydrochloride alone, indications of the formation of a benzodipyrrhole derivative were obtained; but the compound was not formed in quantity sufficient to admit of its purification.

By heating benzoin with orthophenylenediamine hydrochloride, *phenylbenzimidazole*, $C_6H_4\begin{matrix}NH\\ <\\ N\end{matrix}>C\cdot Ph$, was obtained, the benzoin molecule breaking up in the process. Benzoin and free orthophenylenediamine, on the other hand, yielded *diphenylquinoxaline*, $C_6H_4\begin{matrix}N{:}C\cdot Ph\\ <\\ N{:}C\cdot Ph\end{matrix}$, oxidation taking place during the process. The formation of the latter compound in this reaction had, as we afterwards found, been already observed by O. Fischer (*Ber.*, 1891, **24**, 720).

96. "The condensation of ethyl salts of acids of the acetylene series with ketonic compounds." By Siegfried Ruhemann and A. V. Cunnington.

The substitution products of ethyl phenylpropiolate, *e.g.*, ethyl *p*-nitrophenylpropiolate, on treatment with sodium ethoxide, yield, with ethyl acetoacetate and ethyl benzoylacetate respectively, the nitro-

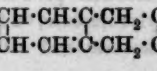
substituted cyclic compounds corresponding to the α-pyrone derivatives previously described. The homologues of ethyl acetoacetate, however, on treatment with ethyl phenylpropiolate and sodium ethoxide, give rise to a mixture of compounds which the authors were unable to separate by fractional distillation. The α-pyrone derivatives obtained from β-diketones, like those from ethyl salts of β-ketonic acids, can be transformed into pyridine derivatives. Thus diphenylaceto-α-pyrone yields  (m. p. 255°). The intermediate product of this reaction, *i.e.*, the ethyl salt, $CO_2Et{\cdot}CH{:}CPh{\cdot}CAc{:}CPh(NH_2)$ (m. p. 161—162°), was isolated.

It was further found that ethylamine, like ammonia, yields, with α-pyrone derivatives, additive compounds with two molecules of the amine. The behaviour of ethyl acetylenedicarboxylate differs from that of ethyl phenylpropiolate towards the ethyl salts of benzoylacetic and acetoacetic acids. In these cases, α-pyrone derivatives are not produced, but compounds which are most probably trimethylene derivatives, such as  , a yellow oil with green fluorescence, b. p. 236—237° at 11 mm., and  a colourless oil, b. p. 186—187, at 13 mm.

97. "Dextro-ac-tetrahydro-β-naphthylamine." By William Jackson Pope.

The only amido-derivative of tetrahydronaphthalene which has previously been resolved into optically active components is ac-1 : 4′-tetrahydronaphthylenediamine; this base was resolved by Bamberger (*Ber.*, 1890, **23**, 291) by crystallising its acid tartrates.

On adding a solution of half a molecular proportion of ammonium dextro-α-bromocamphorsulphonate to a hot aqueous solution of synthetic ac-tetrahydro-β-naphthylamine hydrochloride, and allowing to cool, a copious separation of *dextro-ac-tetrahydro-β-naphthylamine dextro-α-bromocamphorsulphonate*, $C_{10}H_{11}NH_2,C_{10}H_{14}BrOSO_3H$, occurs; this salt is very sparingly soluble in water, but crystallises from a mixture of alcohol and acetone in long, colourless needles melting at 185—187°, and in a 5 per cent. solution in absolute alcohol has the specific rotation $[\alpha]_D = +78°$.

Dextro-ac-tetrahydro-β-naphthylamine,  , is

obtained as a colourless oil on treating its dextrobromocamphorsulphonate with soda, extracting repeatedly with ether, and distilling under reduced pressure. It has the specific rotation $[\alpha]_D = +31°$ at 15° in a 16 per cent. solution in benzene. The *dextrocamphorsulphonate*, $C_{10}H_{11}NH_2,C_{10}H_{14}OSO_3H$, obtained by treating the dextrobase by Reychler's dextrocamphorsulphonic acid, separates from aqueous solution in large, very lustrous, transparent crystals melting at 215—216°; it has the specific rotation $[\alpha]_D = +43{\cdot}5°$ in a 2 per cent. aqueous solution.

98. **"The resolution of racemic tetrahydroparatoluquinaldine into its optically active components." By William Jackson Pope and Edmund Milton Rich.**

The authors have obtained racemic tetrahydroparatoluquinaldine, $\begin{matrix} CMe\cdot CH:C\cdot CH_2\cdot CH_2 \\ \| \qquad\quad | \\ CH\cdot CH:C\cdot NH\cdot CHMe \end{matrix}$, described as an oil by Doebner and Miller (*Ber.*, 1883, **16**, 2464), as a colourless, crystalline substance melting at 32°. It separates in large, transparent crystals from solution in light petroleum, and is almost odourless. The racemic *hydrochloride* crystallises in magnificent prisms melting at 171—173°. Racemic *benzoyltetrahydroparatoluquinaldine*, $C_{11}H_{14}NCOPh$, separates from its solution in acetone in large, colourless crystals melting at 103—104°. On adding half a molecular proportion of ammonium dextro-α-bromocamphorsulphonate in aqueous solution to a solution containing one molecular proportion of racemic tetrahydroparatoluquinaldine hydrochloride, *lævotetrahydroparatoluquinaldine dextro-α-bromocamphorsulphonate*, $C_{11}H_{15}N,C_{10}H_{14}BrOSO_3H$, separates as an oil which soon solidifies; it crystallises from dilute alcohol in colourless needles melting at 195—196°. *Lævotetrahydroparatoluquinaldine*, $C_{11}H_{15}N$, is obtained as a colourless, crystalline mass on treating its dextrobromocamphorsulphonate with dilute soda. It separates from its solution in light petroleum in long, colourless, transparent prisms melting at 52—53° having a scarcely perceptible quinoline-like odour; in a 2 per cent. solution in benzene at 21°, it has the specific rotation $[\alpha]_D = -80{\cdot}9°$ and the molecular rotation $[M]_D = -130{\cdot}2°$. The *hydrochloride* crystallises in magnificent, colourless crystals melting at 192—194°, and in a 2 per cent. aqueous solution at 18° has the specific rotation $[\alpha]_D = -68{\cdot}7°$ and the molecular rotation $[M]_D = -135{\cdot}3°$. *Benzoyllævotetrahydroparatoluquinaldine*, $C_{11}H_{14}NCOPh$, crystallises from alcohol in colourless prisms melting at 100·5°; in a 2 per cent. solution in benzene at 18°, it has the specific rotation $[\alpha]_D = +228{\cdot}8°$ and the molecular rotation $[M]_D = +606{\cdot}4°$. Tetrahydroparatoluquinaldine is homologous with the tetrahydroquin-

aldine recently resolved by Pope and Peachey (*Proc.*, 1899, 15, 124), and the two bases exhibit interesting relationships. Thus dextro-α-bromocamphorsulphonic acid in both cases separates the lævo-base from the externally compensated mixture. Further, in 2 per cent. solutions in benzene, the lævo-bases have the same molecular rotation, viz., $[M]_D = -130{\cdot}2°$. Again, on benzoylating the lævorotatory bases, dextrorotatory benzoyl derivatives are obtained, and these have nearly the same molecular rotations in solution in benzene.

99. "Isomeric salts of hydrindamine containing pentavalent nitrogen." By Frederic Stanley Kipping, D.Sc., F.R.S.

The base, α-hydrindamine, prepared by reducing the oxime of α-hydrindone (König, *Inaug. Diss. Leipzig*, 1889; Kipping and Revis, *Trans.*, 1897, 71, 238), combines with bromocamphorsulphonic acid yielding unequal quantities of two hydrated salts which can be separated by fractional crystallisation. After having been dried at 100°, the more sparingly soluble salt melts at about 150°, the more readily soluble one at about 130°; both compounds have the composition $C_9H_{11}N,C_{10}H_{14}BrO{\cdot}SO_3H$.

Although α-hydrindamine contains an asymmetric carbon atom, and might, therefore, be expected to afford two salts under these conditions, the base regenerated from either of these salts by steam distillation with barium hydrate is optically inactive; the base thus regenerated also gives a hydrochloride and a benzoyl derivative identical in ordinary properties with the corresponding compounds prepared directly from the original externally compensated base. It appears, therefore, that fractional crystallisation of the salt formed with bromocamphorsulphonic acid does not effect a resolution of externally compensated hydrindamine, although this acid has been successfully employed by Pope and Peachey (*Proc.*, 1899, 15, 124) for the separation of the optically isomeric tetrahydroquinaldines.

When, moreover, the base regenerated from one of the isomeric salts is treated with bromocamphorsulphonic acid, it again yields a mixture of the two compounds; the salt of lower melting point is also transformed, partly or entirely, into the isomeride by evaporation with a solution of hydrindamine.

The difference between these two isomerides is not purely crystallographic, since both compounds retain their specific properties on repeated crystallisation from water and other solvents; they have also different specific rotations.

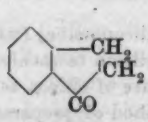
Two different salts, apparently analogous to those just described, are also obtained when hydrindamine is combined with chlorocamphorsulphonic acid, but these two compounds have not yet been studied.

Hydrindamine and lævorotatory *cis*-π-camphanic acid (*Trans.*, 1896, **69**, 943) also combine to form two isomeric anhydrous salts having the composition $C_9H_{11}N,C_{10}H_{14}O_4$; the two compounds can be separated by fractional crystallisation, and, although very similar in appearance, they differ in melting point by about 20°, the more sparingly soluble one melting at about 190°, the other at about 170°. The base regenerated from one of these salts appears to be inactive, and the isomerism of the two compounds seems to be of the same kind as that of the two salts of bromocamphorsulphonic acid. The more readily soluble *cis*-π-camphanate can be converted into the isomeride by evaporation with excess of a solution of hydrindamine; the specific rotations of the two salts are apparently different.

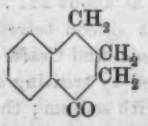
As it is impossible at present to arrive at any final conclusion as to the cause of the existence of the various isomeric salts briefly described in this note, only the more important facts have been recorded. It may be noted also that the assumption, that the isomerism is due to the pentavalent nitrogen atom being in a position in which its free rotation is prevented, explains some of the facts; another possible explanation is, that autoracemation of the free base occurs with great rapidity, but further experimental evidence is required before either view can be accepted.

100. "Synthesis of phenoketoheptamethylene." By F. Stanley Kipping, D.Sc., F.R.S., and Miss L. Hall.

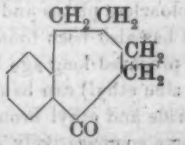
In continuation of previous work on the formation of cycloid ketones (*Trans.*, 1894, **65**, 480; 1899, **75**, 144), the authors have studied the action of aluminium chloride on phenylvaleric chloride, $Ph\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot COCl$, and find that, under suitable conditions, the reaction proceeds in accordance with the equation: $Ph\cdot[CH_2]_4\cdot COCl = HCl + C_{11}H_{12}O$. The product is a ketone, and is in all probability a phenoketoheptamethylene (or phenoheptaphanone) produced by an intramolecular condensation exactly analogous to that which occurs in the formation of α-hydrindone and α-ketotetrahydronaphthalene from the chlorides of phenylpropionic acid and phenylbutyric acid respectively; the relationship between the three cycloid ketones which have now been prepared by this reaction is shown by the following formulæ:



α-Hydrindone.



α-Ketotetrahydronaphthalene.



Phenoketoheptamethylene.

Phenoketoheptamethylene is a colourless liquid having an odour very like that of peppermint; it is volatile in steam and only very sparingly soluble in water. *Phenoketoheptamethylene semicarbazone*, prepared in the usual manner, crystallises in glistening plates melting at about 219°; it is decomposed by dilute sulphuric acid, the ketone being regenerated. The analysis of this compound gave C = 66·4, H = 7·2, the numbers demanded by theory for $C_{15}H_{15}N_3O$ being C = 66·4, H = 6·9 per cent. As the new ketone contains a closed chain of seven carbon atoms attached to the benzene nucleus, and is the first compound of this kind which has been obtained, the authors are making further experiments to confirm their views as to its constitution, and are also investigating its derivatives.

101. "Organic compounds containing silicon." By F. Stanley Kipping, D.Sc., F.R.S., and Lorenzo L. Lloyd.

Since the publication of various papers by Polis (*Ber.*, 1885, **18**, 1542; 1886, **19**, 1012, 1024), very little work has been done on organic compounds containing silicon, more especially as regards those of the aromatic series; the authors, having recently taken up the study of some compounds of this kind, desire to record briefly a few of their results. In the preparation of silicon tetraphenyl by the method described by Polis (*loc. cit.*), a bye-product melting at 148° is usually obtained in small quantities; this substance is triphenylsilicol $(C_6H_5)_3Si{\cdot}OH$, and is doubtless identical with the compound obtained by Polis by decomposing triphenylsilicon chloride with water, in spite of the fact that the melting point assigned to it by Polis is only 139—141°. Triphenylsilicol crystallises in large, transparent prisms, and when boiled with acetic chloride it is converted into *triphenylsilicyl acetate*, $(C_6H_5)_3Si{\cdot}OAc$; the last-named compound forms colourless prisms and melts at 91—92°.

When triphenylsilicol is dissolved in glacial acetic acid and the solution warmed with a little concentrated nitric acid, a colourless, crystalline substance is gradually deposited; this product gave on analysis results agreeing with those required for *triphenylsilicyl ether*, $(C_6H_5)_3Si{\cdot}O{\cdot}Si(C_6H_5)_3$, and as it is also produced by the action of other mineral acids on the alcohol, there is little doubt as to its having this constitution. Triphenylsilicyl ether crystallises from acetic acid in colourless plates and melts at about 221°.

It has also been found that silicon tetrethyl (siliconononane) (which was prepared long ago by Friedel and Crafts from silicon tetrachloride and zinc ethyl) can be obtained by treating a mixture of silicon tetrachloride and ethyl bromide with sodium; this method of preparation being a comparatively easy one, the investigation of silicon tetrethyl

and its derivatives is also being continued. The estimation of the silicon in many of those silicon compounds which volatilise without decomposition is best carried out by heating in a crucible with concentrated sulphuric acid and weighing the residual silica; although this method may not be so generally applicable as that suggested by Polis (*Ber.*, 1886, 19, 1024), it gives very good results in many cases and is very easily carried out.

102. "The velocity of reaction before complete equilibrium." By Meyer Wilderman, B.Sc., Ph.D.

The reactions investigated were the solidification of supercooled liquids and solutions, the separation of the solid from the pure liquid solvent and from its solutions (*e.g.*, velocity of ice separating from pure water and from solutions of various salts), the separation of dissolved substance from supersaturated solutions, the melting of pure solid solvent in the warmer liquid solvent and in solutions, &c. The reactions take place very quickly, some of them lasting only 15 seconds. Advantage was taken of the fact that the above reactions were accompanied by an evolution or an absorption of heat, which is directly proportional to the amount of ice or salt separated. The velocity of ice separation was determined by the rate of change of temperature in the system. A platinum thermometer was used and the deflections of the galvanometer were photographed on a revolving drum. The author finds that the following general equation holds good for all the above reactions, $\frac{dt}{dz} = C(t_0 - t)(t - t_\infty + K)$, where t_0 is the temperature of equilibrium, t_∞ that at which the reaction is started, K an instability constant. In other words, the velocity of reaction at the time z is directly proportional to the remoteness from the state of equilibrium, to the surface of contact of the two reacting parts of the heterogeneous system, and to the instability constant K. Hence a supercooled liquid or supersaturated solution must spontaneously crystallise when a certain limit, indicated by K, is passed. From the above equation, it follows that complete equilibrium is "static," whilst incomplete equilibrium is "dynamic."

103. "The ultraviolet absorption spectra of albuminoids in relation to that of tyrosin." By A. Wynter Blyth.

The author has studied the ultraviolet absorption spectra of egg-albumin, serum albumin, legumin, casein, Schrotter's albumose, certain toxalbumins, and tyrosin. He comes to the conclusion that the absorption band of ordinary albumin is identical with that of tyrosin. Gelatin, Schrotter's albumose, and certain other albuminoid

substances show no band; in these, tyrosin is absent. The author describes a special cell facilitating the study of absorption spectra. A solid block of quartz is cut into steps, the faces of the steps and the back of the quartz being highly polished; the cell is completed by a quartz plate and glass ends; in this way, with one filling, successive thicknesses may be brought before the slit.

104. "An explanation of the laws which govern substitution in the case of benzenoid compounds." (Third Notice.) By Henry E. Armstrong.

This subject was dealt with somewhat fully in two communications made to the Society in 1887 (*Trans.*, **51**, 258, 583). It was then suggested that the formation mainly of meta-di-derivatives from mono-derivatives containing acidic radicles is perhaps due to the production, in the first instance, of a compound in which the acting molecule is associated with the acidic radicle. The object of the present note is to unreservedly withdraw this hypothesis, and to substitute what is believed to be a rational explanation, which has been arrived at after prolonged study of the subject with the assistance especially of Messrs. Berry and Lewis.

Owing to the readiness with which aniline is acted on by various agents, a false idea has been engendered as to the influence of nitrogen on substitution: in reality, it has a very slight predisposing power. Thus, although azobenzene readily forms an unstable perbromide, it is brominated only with difficulty, and is not easily acted on by substituting agents generally. Diazobenzene perbromide and the diazosulphonate from sulphanilic acid manifest complete indifference to bromine. In point of fact, there is little doubt that the activity of aniline and similar amines is the outcome of the presence of hydrogen in the amino-group; and it is even probable—as suggested in the second of these notices—that the formation of ortho- and para-compounds from primary and secondary amines is always preceded by that of the related compound in which hydrogen in the amino-group is displaced. A similar argument is applicable to the phenols, but there is little direct evidence of any prior displacement of the hydrogen of the hydroxyl group. In any case, in the formation of both ortho- and para-compounds from amines and phenols, there is reason to suppose that nitrogen and oxygen respectively act as attractive and also as orienting elements.

On the other hand, when meta-compounds are formed from amino-derivatives, probably it is because the nitrogen is so situated as to be both destitute of attracting power and possessed of ortho- and para-inhibiting power. Evidence of such inhibiting power is afforded by Miss Evans's observation (*Proc.*, 1895, **11**, 235; 1896, **12**, 234) that

when subjected to the action of bromine, dimethylanilineparasulphonic acid yields a mono-derivative which is stable in presence even of a large excess of bromine at ordinary temperatures—a behaviour altogether different from that of anilineparasulphonic acid, which is at once converted into tribromaniline on merely adding bromine to its aqueous solution.

When negative acid radicles are introduced into the amino-group of aniline, a far greater effect is produced than by positive radicles. Thus, when acetylsulphanilic acid is acted on by a single molecular proportion of bromine, at least 50 per cent. of parabromacetanilide is produced, and the monobrominated acid which is simultaneously formed yields practically nothing but dibromacetanilide when acted on by bromine. The behaviour of benzoylsulphanilic acid is similar to that of the acetyl acid.

An equally remarkable effect is produced by alkylating phenolparasulphonic acid. Whereas this acid is converted with extreme facility into the dibromosulphonate and it is difficult to arrest the action at any earlier stage, the methoxy-, ethoxy- and benzyloxy-acids prepared from it yield a large proportion of the monobromophenol *ether* together with monobrominated sulphonate when subjected to the action of only a single molecular proportion of bromine, and when further acted on the monobrominated sulphonates yield dibromophenol ethers. But different radicles produce markedly different effects, the benzylated sulphonate giving little besides the bromo-ether, whereas the methylated and ethylated sulphonate yield about equal proportions of bromo-ether and bromo-sulphonate. The corresponding metacresol derivatives behave in a precisely similar way.

Ortho- and para-nitrophenetolsulphonates also directly exchange the sulphonic group for bromine, no trace of brominated acid being formed; the corresponding phenol acids yield first a bromonitro-acid, and then the dibromonitrophenol.

But phenyl itself apparently exercises the greatest influence when it takes the places of the hydrogen in phenol, phenyl ether para-sulphonic acid, $Ph{\cdot}O{\cdot}C_6H_4{\cdot}SO_3H$, absorbing but a small proportion of bromine, and without the sulphonic group being displaced.

The difference between an alkylated phenol and phenol is therefore similar to that which obtains between dialkylated aniline and aniline, and at least as great: the introduction of a complex radicle in place of aminic or hydroxylic hydrogen, in fact, produces effects which have not been as yet sufficiently considered.

In order to produce meta-derivatives from amines, it is necessary to paralyse as far as possible the ordinary ortho-para-orienting influence of the amino-group, and to give opportunity for the attack to take place in the nucleus; abundant evidence has been obtained that this can be

done in many cases. When acetanilide is acted upon by sulphonating agents, it is initially converted into acetylsulphamic acid, *i.e.*, *sulphamated*; but the sulphamic acid is very prone to undergo change into sulphonic acid, and readily changes into ortho- or para-sulphonic acid, according to the conditions: consequently there is little opportunity for the sulphamic acid to sulphonate, and only traces of meta-acid can be obtained. Sulphamated benzanilide is far more stable, however, and it is easy under appropriate conditions to obtain a large proportion of benzoylmetanilic acid by sulphonating benzanilide; but the action readily proceeds a stage further, the benzoyl also becoming sulphonated. Paracetoluide and orthacetoluide, also readily yield acids in which the sulphonic group is meta- to the nitrogen when the conditions are so chosen as to sulphonate the sulphamate which is initially formed. Again, if parabromacetanilide be cautiously dissolved in strongly fuming acid, and the solution be poured on ice and the liquid boiled, a product rich in ortho-acid is obtained; but if the sulphonation be less carefully conducted, so as to give opportunity for all the sulphamate to sulphonate, pure meta-acid is eventually obtained. Both 2:4- and 2:6-dibromacetanilide give meta-acid with far greater facility, the sulphamate in these cases being very insensitive to change, so that the ortho-acid is obtained from the one and the para-acid from the other only by heating the sulphate of the amine at about 180°.

In the case of phenol, although when deprived of the company of hydrogen oxygen acquires marked inhibitory powers, being destitute of basic properties, it cannot be rendered sufficiently unattractive to prevent its exercising ortho- and para-orienting power, consequently phenolic compounds do not yield meta-derivatives. But it is very noteworthy that 2:6-dibromophenetol is converted into a polysulphonic acid with exceptional facility, just as dimethyl- and diethyl-aniline yield, the one a tetra-, the other a penta-derivative when brominated, although aniline yields only tribromaniline.

Briefly stated, the view now advocated is that in compounds which ordinarily furnish meta-di-derivatives, the radicle (NO_2, CO_2H, &c.) is not only unattractive and possessed of little or no ortho-para-orienting power, but even exercises an inhibiting influence on these positions: consequently, when the two elements of any substituting agent become associated with positions 3 and 4 of the benzene nucleus, separation takes place from 4 rather than from 3, and therefore the meta-derivative is the chief product. The very numerous points of detail which require discussion will be dealt with in a paper in which the results alluded to in the course of this abstract and many others will be fully displayed.

105. "The colouring matters of dyer's broom and heather." By A. G. Perkin and F. G. Newbury.

The *Genista tinctoria* (dyer's broom), a yellow dyestuff formerly of some importance, contains two colouring matters, the first identical with the luteolin of weld (*Reseda luteola*), and the second, a new colouring matter, *genistein*. The latter has a composition corresponding to the formula $C_{14}H_{10}O_5$, colourless needles, and yields an acetyl derivative, $C_{14}H_7O_5(C_2H_3O)_3$, m. p. 197—201°, and a tetrabromo-compound, $C_{14}H_6Br_4O_5$, colourless needles melting above 290°. On decomposition with alkali, it gives phloroglucinol and an acid of the formula $C_8H_8O_3$, m. p. 147—149°; this, with fused alkali, forms parahydroxybenzoic acid, and appears to be *parahydroxyphenylacetic acid*. *Genistein dimethylether*, colourless leaflets, m. p. 137—139°, is insoluble in alkaline solutions, but forms a *monacetyl derivative* of the formula $C_{14}H_7O_3(OCH_3)_2 \cdot Ac$, fine needles, m. p. 202—204°. A second product of the methylation, formed in minute quantity, melts at 187—189°, and appears to be isomeric with the above ether. In dyeing property, genistein closely resembles apigenin and vitexin, and to it the constitution of a *trihydroxyphenylketocumaran*, $(OH)_2 \cdot C_6H_2 \langle \begin{matrix} O \\ CO \end{matrix} \rangle CH \cdot C_6H_4(OH)$, has been provisionally assigned. The colouring matter of *Calluna vulgaris* (heather) is quercetin, and there is also present a catechol-tannin in small quantity.

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PROCEEDINGS

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Vol. 15. No. 213.

The following are the abstracts of papers received during the vacation, and published in the *Transactions*:—

106. **"Researches on the alkyl-substituted succinic acids. Part I. Methods of preparation." By William A. Bone and Charles H. G. Sprankling.**

These acids may be prepared in quantity from the ethyl cyanosuccinates produced by the interaction of ethyl cyanacetate and the esters of α-brom- fatty acids (*Proc.*, 1899, 15, 5).

An account is given of the properties of the ethyl methylcyanosuccinates, the corresponding methylsuccinic acids, their characteristic anhydrides, anilic acids, and calcium salts.

107. **"Some derivatives of dibenzyl ketone." By Francis E. Francis, B.Sc., Ph.D.**

Following R. Schiff's work on the interaction of benzal-aniline and acetoacetic ester and similar ketones, three isomeric addition products were obtained when dibenzyl ketone was employed. The first is produced by the action of corresponding amounts of the ketone and benzal-aniline, the second when the reaction takes place in the presence of traces of piperidine, and the third by the action of a trace of sodium ethoxide on either of the addition compounds obtained in the preceding reactions. No colour reaction with ferric chloride is given by either the ketone or any of the three isomeric substances. Like dibenzyl ketone, desoxybenzoin when treated with benzal-aniline, gives three substances corresponding to the above, but, unlike it, it

gives a fourth with piperidine, which is much less soluble and possesses a much higher melting point than the others. The oxime and hydrazone, and the compounds formed by the action of ammonia and aniline on monobromodibenzyl ketone, are described.

108. "Action of light and of oxygen on dibenzyl ketone." By Emily C. Fortey, B.Sc.

When dibenzyl ketone is exposed to air in presence of sunlight, partial decomposition takes place with formation of benzaldehyde, benzoic acid, and phenylacetic acid. After prolonged exposure of a sealed tube containing the ketone with oxygen, another reaction was found to have taken place, carbon monoxide and toluene being produced, together with a substance melting at 193—194° and having a composition corresponding with the formula $C_{15}H_{13}O$. These products were also formed when dibenzyl ketone was exposed in vacuous tubes or tubes filled with carbon dioxide.

109. "The vapour pressures, specific volumes, and critical constants of hexamethylene." By Sydney Young, D.Sc., F.R.S., and Emily C. Fortey, B.Sc.

A specimen of hexamethylene obtained by fractional distillation from Galician petroleum was found to solidify, though not completely in an ordinary freezing mixture. It was therefore still further purified by fractional crystallisation until the melting point rose to 4·7°. The density of the liquid at 0°/4° was 0·79675, b. p. 80·9°, at 760 mm. The vapour pressures, specific volumes, and critical constants were determined; the latter are: critical temperature = 280·0°, critical pressure = 30252 mm., critical volume of a gram = 3·659.

110. "The composition and tensions of dissociation of the ammoniacal chlorides of cadmium." By Wm. R. Lang, D.Sc., and Albert Rigaut.

This paper gives the results of experiments on the compounds formed by cadmium chloride with ammonia. The compound formed by the action of liquid ammonia at a temperature of −70° has the formula, $CdCl_2,6NH_3$. This substance, heated to 100°, loses ammonia becoming $CdCl_2,2NH_3$, which is extremely stable like the corresponding salt of zinc, and begins to decompose at 210°, whilst at 360° decomposition is still incomplete. By the action of a solution of ammonia, the diammoniacal compound is always obtained; if the hexammoniacal and those intermediate are required, gaseous ammonia

must be passed into the solution. The tensions of these compounds, at temperatures varying from 0° to 70°, were measured; they show that at 60° the hexammoniacal compound ceases to exist and, consequently, for the possible penta-, tetra-, and tri-ammoniacal compounds, temperatures between 60° and 100° must be employed.

111. "The aluminium–mercury couple. I. Action of sulphur chloride on some hydrocarbons in presence of the couple." By Julius B. Cohen and Frederick W. Skirrow.

It has been shown by Hirst and Cohen (*Trans.*, 1895, 67, 826) that the action of the aluminium–mercury couple closely resembles that of aluminium chloride (Friedel and Crafts, *Ann. Chim. Phys.*, 1884, [vi], 1, 520). The authors find that the couple is capable of wide application both as a condensing agent and as a halogen carrier. Sulphur chloride (S_2Cl_2) acts vigorously on the aromatic hydrocarbons in presence of the couple forming the disulphides. *Diphenylene disulphide*, $C_6H_4{:}S_2{:}C_6H_4$, and *ditoluylene disulphide*, $C_7H_6{:}S_2{:}C_7H_6$, were prepared in this way.

Dixylylene disulphide yields, on distillation, xylyl hydrosulphide, a liquid with a low boiling point. The corresponding cumene compound forms a crystalline sulphhydrate, $C_9H_{11}SH$, m. p. 87—90°. A compound probably identical with this is obtained from pseudocumylene disulphide together with the sulphide $(C_9H_{11})_2S$, m. p. 110—111°. The products obtained by the distillation of dicymylene disulphide are liquid and consist of a mixture of the sulphide and hydrosulphide. Sulphur chloride also acts on heptane in presence of the couple; but the product could not be crystallised.

112. "The aluminium–mercury couple. II. The action of bromine on organic compounds in presence of the couple." By Julius B. Cohen and Henry D. Dakin.

The aluminium–mercury couple may be used as a bromine carrier. In presence of small quantities of the couple, bromine forms substitution products with the aromatic hydrocarbons and with the paraffins, very satisfactory yields being obtained. The following substances were prepared in this way: bromobenzene, C_6H_5Br; bromotoluene, C_6H_4MeBr; bromo-*m*-xylene, $C_6H_3Me_2Br$; chlorobromobenzene, C_6H_4ClBr, from chlorobenzene; bromo-*p*-chlorotoluene, $C_6H_3MeClBr$, from *p*-chlorotoluene; *p*-dibromobenzene, $C_6H_4Br_2$, from bromobenzene; 1 : 2 : 4 : 5-tetrabromobenzene, $C_6H_2Br_4$, and hexabromobenzene, C_6Br_6, from dibromobenzene, and dibromochlorotoluene,

$C_6H_2MeClBr_2$, from bromo-*p*-chlorotoluene. Heptyl bromide, tetrabromoheptane, $C_7H_{12}Br_4$, and a third product, isomeric or polymeric with the latter, were obtained from heptane.

113. "Experiments on the constitution of isocamphoronic acid." By W. H. Perkin, jun., and Jocelyn Field Thorpe.

During the course of experiments on the synthesis of isocamphoronic acid, the authors have prepared a substance of the constitution $CO_2H\cdot CH_2\cdot CMe_2\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$, which Baeyer suggested as probably representing this acid, but they find that their synthetical acid is not identical with isocamphoronic acid.

When the sodium derivative of ethyl cyanodimethylglutarate, $CO_2Et\cdot C(CN)Na\cdot CMe_2\cdot CH_2\cdot CO_2Et$ (compare *Trans.*, 1899, **75**, 63), is digested with ethyl bromacetate, *ethyl cyanodimethylbutanetricarboxylate*, $\begin{matrix}CO_2Et\cdot C(CN)\cdot CMe_2\cdot CH_2\\ \quad\quad\quad\

is converted on hydrolysis into a mixture of the cis- and trans-*phenylbutanetricarboxylic acids*, $CO_2H\cdot CH_2\cdot CHPh\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$. The *trans*-acid crystallises from water in prisms containing $\frac{1}{2}H_2O$, but in the anhydrous condition it is a gum, with properties somewhat similar to those of the dimethylbutanetricarboxylic acid above described. The *cis*-acid melts at 178—180°, and is much more soluble in water than the *trans*-acid.

When treated with acetyl chloride, both acids yield the same anhydro-acid of the probable constitution $\begin{matrix}CO\cdot CH_2\\ |\\ O\text{—}CO\end{matrix}\!\!>\!CH\cdot CHPh\cdot CH_2\cdot CO_2H$, which melts at 134—135°.

115. "Further studies on the acids of the acetylene series." By Siegfried Ruhemann and Alfred V. Cunnington.

Ruhemann and Browning (*Trans.*, 1898, **73**, 723) have shown that the ethyl salts of unsaturated acids combine with piperidine, and that, in the case of ethyl phenylpropiolate, union takes place with great evolution of heat. Diethylamine does not combine with the salt until the mixture is heated to 100°, though like piperidine, it combines with ethyl acetylenedicarboxylate very readily at ordinary temperatures. The compounds thus formed have the general formulæ $\begin{matrix}R\cdot C:CH\cdot CO_2Et\\ |\\ NC_5H_{10}\end{matrix}$ and $\begin{matrix}R\cdot C:CH\cdot CO_2Et\\ |\\ N(Et)_2\end{matrix}$. The authors further show that whilst urea and hydroxylamine react with ethyl phenylpropiolate, forming the ureide, $C_6H_5\cdot C{:}C\cdot CONHCONH_2$ (pale yellow needles, m. p. 220°), and the hydroxamic acid, $C_6H_5\cdot C{:}C\cdot C(NOH)OH$ (colourless needles, m. p. 168—169°) respectively, benzamidine produces a cyclic compound (yellow needles, m. p. 274°), either $\begin{matrix}C_6H_5\cdot CH:C\text{—}CO\\ \quad\ |\quad\ |\\ \quad N\quad NH\\ \quad\ \diagdown\ /\\ \quad\ C\cdot C_6H_5\end{matrix}$ or $\begin{matrix}C_6H_5\cdot CH:C\text{—}CO\\ \quad\ |\quad\ |\\ \quad HN\quad N\\ \quad\ \diagdown\ /\\ \quad\ C\cdot C_6H_5\end{matrix}$ benzal-phenyl-glyoxalidone. They have also studied the additive products obtained by the action of bromine on ethyl phenylpropiolate and ethyl acetylenedicarboxylate (*i.e.*, ethyl dibromocinnamate and ethyl dibromomaleate respectively), and point out the remarkable difference in their stability. Ethyl sodiomalonate does not react with ethyl dibromocinnamate, but it does with ethyl dibromomaleate. This action, however, does not occur in the manner stated by G. Pum (*Monats.*, 1888, **9**, 446), who supposed that ethyl dimalonylmaleate was formed according to the equation

$$\begin{matrix}EtO_2C\cdot CBr\\ \|\\ EtO_2C\cdot CBr\end{matrix} + 2NaCH(CO_2Et)_2 = \begin{matrix}EtO_2C\cdot C\cdot CH(CO_2Et)_2\\ \|\\ EtO_2C\cdot C\cdot CH(CO_2Et)_2\end{matrix} + 2NaBr.$$

The authors prove that this substance is nothing but ethyl ethanetetracarboxylate, which is produced thus:

$$\begin{matrix}EtO_2C\cdot CBr\\ \|\\ EtO_2C\cdot CBr\end{matrix} + 2NaCH(CO_2Et)_2 = \begin{matrix}EtO_2C\cdot C\\ \|\\ EtO_2C\cdot C\end{matrix} + \begin{matrix}CH(CO_2Et)_2\\ |\\ CH(CO_2Et)_2\end{matrix} + 2NaBr.$$

The ethyl acetylenedicarboxylate appearing in the equation unites with the ethyl malonate present and forms ethyl propenetetracarboxylate, $\begin{matrix}CH(CO_2Et)\\ \|\\ CCO_2Et\\ |\\ CH(CO_2Et)_2\end{matrix}$. This result shows that the substances obtained by Pum from his so-called ethyl dimalonylmaleate are the well-known products of the transformation of ethyl ethanetetracarboxylate. His dimalonylmaleic acid is ethenyltricarboxylic acid, and his diglycolylmaleic acid appears, therefore, to be succinic acid.

116. "A contribution to the chemistry of the mandelic acids." By Alex. McKenzie, M.A., D.Sc.

The work was undertaken in order to obtain *d*- and *l*-mandelic acids for the preparation of the optically active phenylalkyloxyacetic acids recently described by the author (*Trans.*, 1899, 75, 753). Although recourse was eventually had to amygdalin as a convenient source of *l*-mandelic acid, the results with mandelic acid are given in view of the attention at present directed to the general subject.

Inactive mandelic acid was resolved on the large scale by use of quinidine and cinchonine. From the pure *d*- and *l*-acids so obtained, the salts of cinchonine, cinchonidine, quinine, quinidine, strychnine, brucine, and morphine were prepared, solubility determinations of which showed that the acid can be conveniently resolved into its optically active components by quinine, or, better, by morphine in alcoholic solution.

A number of metallic salts of the mandelic acids were prepared with the view of ascertaining whether any of them would lend themselves to separation by crystallisation. The attempts to obtain the separation of one enantiomorph by spontaneous crystallisation were unsuccessful, owing, the author supposes, to the "transition temperature" not having been reached, or to hemihedrism being absent or masked in the crystals of the active isomers.

117. "Non-existence of the so-called 'suboxide of phosphorus.'" By David Leonard Chapman and F. Austin Lidbury.

The authors have examined specimens of the supposed suboxide, prepared by the methods of Goldschmidt and Reinitzer, and of Michaelis and Pitsch, and have compared their physical and chemical

properties with those of red phosphorus in a finely divided state, prepared by the action of sunlight on a strong solution of phosphorus in carbon disulphide. They find complete coincidence of properties in both cases; and it is pointed out that no physical or chemical property has yet been observed by which these substances may be distinguished from one another. Analyses show that when purified as completely as possible, the percentage of phosphorus is greater in all cases than the formula P_4O demands; the impurities in the phosphorus being due chiefly to the presence of acids of phosphorus formed by the action of water during preparation.

They conclude that the so-called suboxide is only an impure form of red phosphorus.

118. "The chlorine derivatives of pyridine. Part III. The interaction of chlorine and pyridine hydrochloride." By W. J. Sell, M.A., F.I.C., and F. W. Dootson, M.A.

The authors have previously described a method of obtaining a considerable number of the chloropyridines (*Trans.*, 1898, **63**, 432). With a view to simplifying the method and increasing the yield, they have examined the action of chlorine on pyridine hydrochloride, and succeeded in obtaining (1) a dichloropyridine not hitherto obtained by them, (2) a tetrachloropyridine, in large quantity, melting at 21—22°, (3) pentachloropyridine, (4) an aminotrichloropyridine, and (5) a compound of the empirical formula $C_{10}Cl_{11}HN_2$ and certain of its derivatives.

The substance (5), which is formed in considerable quantity, is regarded as being derived from two pyridine nuclei, and is still under examination.

119. "Amidoamidines of the naphthalene series." By Raphael Meldola and Percy P. Phillips.

The authors have continued the investigation of the ethenyltriamidonaphthalene described in 1887 (Meldola and F. W. Streatfeild, *Trans.*, **51**, 691). The acetyl and benzoyl derivatives are described, and the acid character of the NH-group of the amidine ring is made known by the formation of a silver compound and the corresponding N-methyl derivative. The diazotisable character of the NH_2-group has been further studied, and it is shown that the amidoamine is also capable of combining with diazonium salts of other bases. The products do not appear to be simply diazoamido- or amido-azo-compounds as might have been expected from their mode of formation. The investigation of the latter is being continued.

November 2nd, 1899. Dr. W. H. Perkin, F.R.S., Vice-President, in the Chair.

Messrs. F. J. Beale, George Young, H. Royal-Dawson, E. T. Shelbourn, S. J. Peachey, H. A. Thiersch, R. W. Lindsay, S. Dickson, F. N. A. Fleischmann, and C. Simmonds were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. James William Anderson, 1, Preston Villas, Halling, Kent; Francis Paul Armitage, High House, Brook Green, Hammersmith, W.; Frederick William Armstrong, The Hill, Langport, Somerset; Frederic Arnold Beesley, Bank House, Wirksworth, Derby; Edgar Marsh Chapman, 17, Bloomsbury Square, W.C.; John Arthur Dewhirst, 125, Mount View Road, Stroud Green, N.; Frank Rawlinson Dudderidge, 45, Sidney Grove, Newcastle-on-Tyne; Herbert Frederick Francis Burdett Fermor, 15, Ansdell Road, Peckham, S.E.; Elliott Henry Gurney, Albert Street, Marrickville, New South Wales; Henry Wulff Kinnersley, 4, The Avenue, Keynsham, Somerset; William Thomas Leeming, 60, Lomeshaye Road, Nelson; Stephen Joshua Lett, 25, Percy Street, Liverpool; Edward Watkin Lewis, 64, Ommaney Road, New Cross, S.E.; Wm. D. McCreath, The Plains, Totnes, S. Devon; Harry Ainley Neale, Brentwood, Clothorn Road, Didsbury, Manchester; Thomas Henry Palmer, "Amalfi," Longueville, Sydney, New South Wales; Marchant Pearson, The Grammar School, Bridlington; Bennett C. Polkinghorne, 46, Lynette Avenue, Clapham Common, S.W.; Georges Ponthieu, Pharmacie Centrale de France, Avenue de Paris, St. Denis, Seine; William Downing Raynor, 13, Christ Church Road, Doncaster; Christopher Foulis Roundell, Guards' Club, Pall Mall, S.W.; William Russell, Thetford, Norfolk; Robert Hawks Walton, 424, Park Road, Moore Park, Sydney, N.S.W.; F. R. Leyland Wilson, Charterhouse, Godalming; John Wilson, 73, Melford Road, Leytonstone, E.

The chairman referred to the great loss the Society had sustained through the deaths of its illustrious former President, Sir Edward Frankland, and its Foreign Member, Professor Bunsen.

Of the following papers, those marked * were read:—

*120. "On methods for determining the relative proportions of gaseous chloroform and air in a mixture of the two, and on a method for producing a mixture of air and chloroform in any desired proportion." By A. Vernon Harcourt.

To produce anæsthesia, air is inhaled mixed with a small percentage of chloroform vapour. The proportion of chloroform most suitable

for this purpose has not been determined, probably for want of a good chemical method of making this determination. The reaction which takes place between chloroform and a hot alcoholic solution of potash, $CHCl_3 + 4KOH = 3KCl + HCO_2K + 2H_2O$, seemed to furnish a basis for such a method. However, with regard to this reaction, two statements have been made, that all the chlorine of chloroform can thus be converted into a chloride and that it cannot. The author has worked out and described a method for removing chloroform vapour from air, and obtaining chloride from it by means of the above reaction; but on applying the method to weighed quantities of chloroform the results were always about 4 per cent. too low. This error is so nearly constant that the method may be used, and the results increased by 4 per cent.

A better method depending on a reaction (which, as far as the author knows, is new) has since been worked out by him.

When the mixture of air and chloroform is mixed with a certain proportion of steam by heating it with a few c.c. of water to 50° or 60°, and a platinum wire is kept in a state of incandescence in this mixture, the whole of the chloroform undergoes the following change: $2CHCl_3 + 2H_2O + O_2 = 6HCl + 2CO_2$. With a fairly bright wire the change is complete in an hour, and the hydrogen chloride may be obtained in dilute solution by bringing in 20 c.c. of water, and may be determined in the flask with a standard solution of ammonia. If enough steam is not present, or the platinum wire is not heated beyond a low incandescence, or sufficient time is not allowed, a smell of chlorine will be observed at the mouth of the flask and the result will be too low. It was ascertained incidentally that a weighed quantity of chlorine, treated as above, is completely converted into hydrogen chloride. Doubtless the changes $2H_2O + 2Cl_2 \rightleftharpoons 4HCl + O_2$ both occur, but the water present gradually withdraws all hydrogen chloride from the system.

The author also described a method of producing a mixture of air and chloroform in any desired proportion and of constant composition. This consisted in blowing air through a mixture of chloroform and alcohol. The density of the liquid, showing the proportion of its ingredients, could be observed during the passage of the air by means of two little glass bulbs, of which one floated and one sank when the density was right, and be adjusted by additions of chloroform. Density and temperature being constant, the proportion of chloroform taken up by the air was constant also. To remove alcohol vapour, the current of air was then passed through two wash-bottles containing sulphuric acid and water respectively.

Discussion.

In reply to remarks by Mr. Hehner and Dr. Perkin, Mr. Harcourt said he doubted whether the use of a Lux' balance for observing the density of the gas-stream would be as convenient as the Wolfe's bottle with two floats which he had used. The great difference in density of alcohol and chloroform made the density of the liquid in this case a good index of its composition. He thought a liquid less volatile than alcohol might be found and might have advantages; but alcohol answered well, was innocuous even if a little of its vapour passed on, and could easily be got pure.

***121. "The theory of saponification." By J. Lewkowitsch.**

The author showed that the view of the theory of saponification, according to which the hydrolysis of triglycerides is considered a tetramolecular reaction, must be abandoned in favour of the theory propounded by Geitel, who regards the reaction as bimolecular. If this be so, diglycerides and monoglycerides should occur in partially hydrolysed fats. The author has demonstrated their presence by acetylating the intermediate products, freed from glycerol, and proving that the acetylated products exhibit considerable acetyl values, which rise and fall with the progress of saponification. Additional proof was obtained by determining the amounts of the insoluble fatty acids of the acetylated products, and also their saponification values. The curves illustrating these two series of values correspond to the acetyl curves in a very satisfactory manner.

Discussion.

Dr. Lewkowitsch said, in reply to questions from Mr. Blount and Mr. Hehner, that he had not tried any other methods beyond those mentioned, as, in his opinion, they were sufficient to give a satisfactory answer to the point at issue. The proportion of glycerine in the partially saponified samples might have been determined as a further proof, but the methods employed were shorter and more reliable. The saponification had been carried out in a manner corresponding to operations on a large scale, and since the steam pressure alone causes a very violent boiling and mixing of the mass, there could be little doubt that the samples taken did represent the average. He had not made use of water as a saponifying agent.

***122. "Note on the action of dilute nitric acid upon oleic and elaidic acids." By F. G. Edmed, B.Sc.**

In the course of some experiments on the oxidising action of nitric acid upon oleic acid, the author found that, by using nitric acid of

sp. gr. 1·2—1·3, the sole action was an isomeric change from oleic to elaidic acid. If the density of the acid did not exceed 1·25 and the action took place in the cold, the yield of elaidic acid was quantitative. Increase in the strength of the nitric acid and rise of temperature diminished the yield. The rapidity of the change was dependent on the purity of the oleic acid. The dilute nitric acid used in the experiments was carefully freed by prolonged boiling from nitrous acid, which is known to bring about a similar change.

Nitric acid of the strengths indicated above has no action in the cold upon elaidic acid itself. Hot concentrated nitric acid decomposes it only upon prolonged boiling.

Discussion.

Mr. Edmed said in reply to Dr. Lewkowitsch that the specimen of elaidic acid thus prepared melted at 45° C.

***123. "Formation of tetrazoline." By S. Ruhemann and H. E. Stapleton.**

On heating monoformylhydrazide at 210—220° for about 6 hours, the authors obtained a good yield of tetrazoline, $CH\langle^{NH\cdot N}_{N\cdot NH}\rangle CH$. The hydrochloride of this base, $C_2H_4N_4,HCl$, had been prepared recently by Pellizzari (*Atti R. Accad. dei Lincei*, 1899, [v], 8, I, 327) by heating diformylhydrazide and treating the crystalline product thus formed with hydrochloric acid. The authors find the melting point of this salt to be 151—152°. The free base is extremely soluble in alcohol and in chloroform, sparingly so in petroleum-ether. It crystallises from a mixture of chloroform and alcohol in colourless needles which melt at 82—83°, are very deliquescent, and give with copper sulphate a blue coloration. The picrate, $C_2H_4N_4,C_6H_2(NO_2)_3OH$, forms yellow prisms, soluble in alcohol only with great difficulty.

Discussion.

Dr. George Young said that the authors of this paper had discarded the name dihydrotetrazine in favour of tetrazoline, the term introduced by Pellizzari. This was to be regretted as tending to confusion in the nomenclature of the carbo-nitrogen cyclic compounds. Dihydropyrrole was known as pyrroline, dihydropyrazole as pyrazoline. Tetrazoline should denote dihydrotetrazole, and not dihydrotetrazine. The name isotetrazoline was in use for certain dihydro-derivatives of tetrazole.

Mr. Stapleton, in reply, said that although the alteration by

Pellizzari of the name dihydrotetrazine into tetrazoline was perhaps not altogether satisfactory, it had been accepted both by Pinner and Bamberger, and accordingly the authors of the paper had not hesitated to employ the term.

***124. "Asymmetric optically active nitrogen compounds. Dextro- and lævo-benzylphenylallylmethylammonium iodides and bromides." By William Jackson Pope and Stanley John Peachey.**

On heating the α-benzylphenylallylmethylammonium iodide prepared by Wedekind (*Ber.*, 1899, **32**, 517) with one molecular proportion of silver dextrocamphorsulphonate dissolved in acetone and ethyl acetate, filtering, and evaporating to dryness, a crystalline residue was obtained which by fractional crystallisation from solution in acetone and ethyl acetate, may be resolved into the less soluble constituent, *dextro-α-benzylphenylallylmethylammonium dextrocamphorsulphonate*, $N(C_7H_7)Ph(C_3H_5)MeC_{10}H_{15}OSO_3$, and the more soluble isomeric dextrocamphorsulphonate of the *lævo-base*; the former has the molecular rotation in aqueous solution $[M]_D = +208°$ and the latter $[M]_D = -87°$.

On adding potassium iodide or bromide to aqueous solutions of these salts, the corresponding iodide or bromide is precipitated, and may be purified by crystallisation from alcohol; the following salts were thus obtained. *Dextro-α-benzylphenylallylmethylammonium iodide*, $N(C_7H_7)Ph(C_3H_5)MeI$, $[\alpha]_D = +52{\cdot}4°$. *Dextro-α-benzylphenylallylmethylammonium bromide*, $N(C_7H_7)Ph(C_3H_5)MeBr$, $[\alpha]_D = +68{\cdot}6$. *Lævo-α-benzylphenylallylmethylammonium iodide*, $[\alpha]_D = -51{\cdot}4°$. *Lævo-α-benzylphenylallylmethylammonium bromide* $[\alpha]_D = -67{\cdot}3°$.

The isolation of these compounds proves that dissolved substances may owe their optical activity to the asymmetry of nitrogen.

It is further shown that Wedekind's iodide is not a racemic compound, but merely an ordinary or pseudoracemic mixture of the dextro- and lævo-components.

Discussion.

Dr. Armstrong thought this communication was the most valuable contribution made to stereochemistry since the introduction of geometrical considerations by Le Bel and van't Hoff.

The discovery of a method of preparing asymmetric nitrogen compounds was not only of intrinsic importance, but afforded a means of investigating the problem which chemists had so long disputed as to the valency of nitrogen in ammonium compounds. It would perhaps be possible by varying the number of radicles to discriminate between

compounds containing pentad and "molecular" compounds containing triad nitrogen.

Dr. LEWKOWITSCH said he fully appreciated the difficulties attendant on work of this kind, as some time ago he had attempted to prepare silicon compounds possessing optical activity, but so far without success. He ventured to suggest that these experiments might now be resumed.

125. "Camphoroxime. Part III. Behaviour of camphoroxime towards potassium hypobromite." By M. O. Forster, Ph.D., D.Sc.

With the object of preparing brominated derivatives of camphoroxime, the author has studied the behaviour of this substance towards alkaline hypobromite.

The *compound*, $C_{10}H_{16}BrNO_2$, obtained by the action of a concentrated ice-cold solution of potassium hypobromite on camphoroxime, crystallises from alcohol in snow-white, fern-like aggregates, and melts at 220° to a colourless liquid which immediately decomposes; it gives Liebermann's reaction for nitroso-derivatives, and yields camphoroxime on reduction with zinc dust and acetic acid. A two per cent. solution in benzene gave $[\alpha]_D = -65{\cdot}6°$.

The *compound*, $C_{10}H_{14}BrNO$, produced when the foregoing substance is dissolved in concentrated sulphuric acid, crystallises from alcohol in lustrous, transparent prisms; it shrinks and darkens at about 210°, becoming completely charred at 220°. This derivative is optically inactive, and does not give Liebermann's reaction. Treatment with hot, concentrated hydrochloric acid converts it into an *isomeride*, which separates from alcohol in large, transparent, six-sided crystals, and melts to a colourless liquid at 240°; this modification is likewise optically inactive, and does not give Liebermann's reaction; it yields a *benzoyl* derivative, which crystallises from alcohol in lustrous scales melting at 174—176°.

The *nitrile*, $C_9H_{13}N$, obtained when either of the compounds, $C_{10}H_{14}BrNO$, is heated with aqueous soda, forms a limpid, fragrant oil which boils at 198—199° under 760 mm. pressure, and has sp. gr. 0·9038 at 24°; it is oxidised by an ice-cold solution of potassium permanganate, and instantly decolorises a solution of bromine in chloroform.

The *amide*, $C_9H_{15}NO$, occurs as a bye-product in the preparation of the nitrile, and is formed when that substance is heated with alcoholic potash; it crystallises from light petroleum in white, highly lustrous needles melting at 90°. When this compound is heated with hydrochloric acid, isolauronolamide and isolauronolic acid are produced, and as campholytic acid is converted by mineral acids into isolauronolic

acid, it appears probable that the new amide is the hitherto unknown amide of campholytic acid. Experiments are being conducted with the view of ascertaining if this is so.

126. "Optical influence of an unsaturated linkage on certain derivatives of bornylamine." By M. O. Forster.

Condensation products of bornylamine with aromatic aldehydes have been prepared in order to compare the optical activity of such compounds with the corresponding derivatives of benzylbornylamine.

It is found that transition from benzylbornylamine and its nitro-derivatives to the corresponding benzylidene compounds is attended by a fall in the rotatory power of the benzene and alcoholic solutions; the decrease in the case of the paranitro-derivatives approximates to the rotational difference between benzylbornylamine and benzylidene-bornylamine, but is widely divergent from this in the case of the orthonitro-compounds.

Benzylidenebornylamine, *o-nitrobenzylidenebornylamine*, *p-nitrobenzylidenebornylamine*, *o-hydroxybenzylidenebornylamine*, and *p-hydroxybenzylidenebornylamine* are described in the paper.

127. "The interaction of sodium hydroxide and benzaldehyde." By Charles A. Kohn, B.Sc., Ph.D., and W. Trantom, B.Sc., Ph.D.

The object of the investigation was to ascertain if an intermediate compound was formed in the preparation of benzyl alcohol from benzaldehyde and soda. The authors state, that in presence of water, the sole products of the reaction are benzyl alcohol and sodium benzoate. By employing carefully dried materials, however, benzyl benzoate is formed to the extent of 10 per cent. The reactions which occur are explained by the following equations:—

(1), $2C_6H_5\cdot CHO + NaOH = C_6H_5\cdot C(ONa)(OH)(OC_7H_7)$;

(2), $C_6H_5\cdot C(ONa)(OH)(OC_7H_7) = C_6H_5CO_2Na + C_7H_7OH$;

(3), $C_6H_5\cdot C(ONa)(OH)(OC_7H_7) = C_6H_5\cdot CO_2C_7H_7 + NaOH$.

Reaction (2) is favoured by the presence of water and excess of soda; reaction (3) by an excess of aldehyde.

128. "Electrolytic preparation of induline dyes." By E. C. Szarvasy, Ph.D.

When a mixture of aniline hydrochloride and aniline is fused and electrolysed under given conditions, induline colouring matters are formed. The author describes the apparatus he constructed to carry out these experiments. The following products were separated:

Induline, $C_{18}H_{12}N_3$; B4, anilidoinduline, $C_{24}H_{16}N_4$; induline 6B, $C_{30}H_{23}N_5$; and azophenine, $C_{36}H_{29}N_5$.

The results prove (1) that the chlorine produced by the electrolytic decomposition of the aniline hydrochloride effects diazotisation, (2) that under certain conditions the azo-compounds thus formed react with the hydrochloride of aniline, forming (3) primarily azophenine, (4) ultimately indulines.

129. "The heat of combination of copper with zinc." By T. J. Baker, B.Sc.

The only work in this direction hitherto appears to be by Dr. Galt (*Rep. Brit. Ass.*, 1898, and *Proc. Roy. Soc. Edin.*, 1899) and by Herschkowitsch (*Zeit. f. phys. Chem.*, 1898, **27**, 123). Neither appeared until this work was nearly completed, and in each case the number of observations appears to have been small. In the present research, the method consisted in the determination of the difference between the heat of solution of an alloy of the two metals and that of an equal weight of a mixture in the same proportions. Actual determinations of the latter quantity were made, as it was not found possible to calculate it exactly from the heat of solution of the separate metals.

Two solvents were used. (*a*) Chlorine water (0·15 normal). (*b*) $HNO_3,3H_2O$.

Only alloys with less than 42 per cent. copper could be so finely powdered as to dissolve quickly in chlorine water. With nitric acid as solvent, a series of 21 alloys (all made from the purest metals obtainable and carefully analysed) was examined. The results obtained by both methods agree very well.

The results are expressed in the form of a curve with percentages of copper as abscissæ and heats of formation of 1 gram of alloy as ordinates. From 0 to 30 per cent. of copper, no heat of combination could be detected. This renders doubtful the existence of the supposed compound, $CuZn_2$ (Laurie, Charpy, and Herschkowitsch).

From 30 to 62 per cent. of copper, the curve rises to an ill-defined maximum of 46 calories per gram of alloy. This alloy (62 per cent. copper) does not correspond to any simple atomic compound, but is otherwise remarkable (see 4th Report of the Alloys Research Committee Institution of Mechanical Engineers).

From 62 per cent. copper onwards, the curve gradually sinks to zero at 100 per cent. copper.

Hence copper and zinc evolve heat when alloying with one another, a point of interest with reference to the electro-deposition of brass.

The bearing of these experiments on Lord Kelvin's estimate of the limits of molecular dimensions is briefly discussed.

130. "The action of sulphuric acid on fenchone." By J. E. Marsh.

The author shows that by the action of strong sulphuric acid on fenchone, aceto-xylene (Me : Me : Ac = 1 : 2 : 4) was produced in quantity approximating to the total amount required by theory, and considers this fact to be opposed to the constitution of fenchone recently put forward by Wallach and by Gardner and Cockburn.

131. "On glucosides." By Hugh Ryan, M.A.

By the action of acetochloroglucose on solutions of phenols in alcoholic potash, crystalline glucosides of the β series were obtained.

$\beta\beta$-Naphthol-glucoside, $C_6H_{11}O_5 \cdot OC_{10}H_7$, prepared from acetochloroglucose and β-naphthol, crystallises in long needles [m. p. 184—186°], is easily soluble in alcohol and in hot water, difficultly soluble in acetone, and scarcely soluble in benzene, ligroin, cold water, or ether, is readily hydrolysed either by dilute acids or emulsin, reduces Fehling's solution only after hydrolysis, is stable towards dilute alkali in which it is insoluble, and has a disagreeable taste.

β-p-Cresol-glucoside, m. p. 175—177°, and *β-o-cresol-glucoside*, $C_6H_{11}O_5 \cdot OC_6H_4CH_3$, m. p. 163—165°, resemble one another as well as naphthol-glucoside, crystallising from water in needles which are scarcely soluble in ether, benzene, or ligroin, but are fairly soluble in alcohol and in water, do not reduce Fehling's solution, are readily hydrolysed and possess a bitter taste.

β-Carvacrol-glucoside, m. p. 135°, crystallises from water in needles not readily soluble in ether or cold water, easily soluble in alcohol and in acetone, but scarcely soluble in benzene, chloroform, or ligroin. It does not reduce Fehling's solution, dissolves slowly in dilute alkali, and is hydrolysable by means of dilute acids or emulsin. Its formula is either $C_6H_{11}O_5 \cdot OC_6H_3 \cdot C_3H_7 \cdot CH_3, \frac{1}{2}H_2O$, or $C_6H_{11}O_5 \cdot C_6H_2 \begin{cases} C_3H_7 \\ OH, \frac{1}{2}H_2O \\ CH_3 \end{cases}$.

d-Pentacetyl-glucose (m. p. 110°) is obtained by the action of 20 mols. of acetyl chloride on 1 mol. dry glucose in an open vessel.

Acetochloro-galactose, a colourless semi-solid mass, was got by the action of acetyl chloride on galactose in a closed tube and has been converted into a galactoside of β-naphthol.

132. "Notes on polyazo-compounds." By Raphael Meldola and William Arthur Williams.

Paranitrobenzeneazophenol (Meldola, *Trans.*, 1885, 47, 658) melts at 213—216° if the temperature of the bath is raised rapidly.

The melting point formerly given (184°) is erroneous, and the error has been corrected in the latest edition of Beilstein (vol. 4, p. 1410). The compound has been further characterised by its benzoyl and acetyl derivatives: p-$NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot O \cdot CO \cdot C_6H_5$; slender, orange needles, m. p. 195°. p-$NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot O \cdot CO \cdot CH_3$; dull, orange needles, m. p. 147°. The corresponding amidobenzeazophenol melts at 186° (181° in original description) and forms a difficultly soluble sulphate crystallising in silvery scales having the formula $(p\text{-}NH_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot OH)_2, H_2SO_4 + 3H_2O$.

The base, on acetylation with acetic anhydride and sodium acetate, gives a mixture of a diacetyl with a monacetyl derivative, the latter being phenolic in character: $C_2H_3O \cdot NH \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot OH$; minute, dull orange needles, m. p. 203°; $C_2H_3O \cdot NH \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot O \cdot C_2H_3O$; bright, orange scales, m. p. 236—237°.

The disazo-compound, $C_6H_4(N_2 \cdot C_6H_4 \cdot OH)_2$ (Meldola, *loc. cit.*, 659), does not appear to be crystallisable. Boiling with acetic anhydride and dry sodium acetate results in the formation of the diacetyl derivative, $C_6H_4(N_2 \cdot C_6H_4 \cdot O \cdot C_2H_3O)_2$, which crystallises from nitrobenzene in small, golden-yellow plates melting at 246—248°.

The amidobenzeneazophenol (m. p. 168°) obtained by Wallach and Schulze (*Ber.*, 1882, 15, 3021) by removing the acetyl group from the corresponding acetamido-compound, is the meta-compound isomeric with our para-compound (m. p. 186°).

Para-amidobenzeneazophenol, when treated at a low temperature with a mixture of dilute sulphuric acid and sodium dichromate, undergoes fission in a remarkable way. The azo-group remains attached to the $NH_2 \cdot C_6H_4-$ residue with the formation of a diazodichromate of the complex $NH_2 \cdot C_6H_4 \cdot N_2-$ and the simultaneous oxidation of the $C_6H_4 \cdot OH$ residue to quinone. This mode of decomposition of azo-compounds is being further investigated.

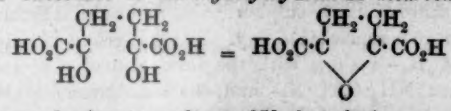
133. "On ethyl dibromobutanetetracarboxylate and the synthesis of tetrahydrofurfuran-$\alpha\alpha'$-dicarboxylic acid." By Bevan Lean, D.Sc., B.A.

A solution of ethyl butanetetracarboxylate in chloroform is readily acted on by bromine with the formation of *ethyl $\alpha\alpha'$-dibromobutanetetracarboxylate*, $\begin{matrix} CH_2 \cdot CBr(CO_2Et)_2 \\ CH_2 \cdot CBr(CO_2Et)_2 \end{matrix}$.

The crystalline dibromo-compound (m. p. 83°) thus obtained, when digested for some hours with a strong solution of barium hydroxide, yields an insoluble barium salt of dihydroxybutanetetracarboxylic acid, $Ba(O_2C)_2C(OH) \cdot CH_2 \cdot CH_2 \cdot C(OH)(CO_2)_2Ba, H_2O$. If this salt is decomposed by sulphuric acid, there results a solution of *dihydroxy-*

butanetetracarboxylic acid, $(HO_2C)_2C(OH)\cdot CH_2\cdot CH_2\cdot C(OH)(CO_2H)_2$. On slowly concentrating the very acrid aqueous solution of this substance over strong sulphuric acid, long needles were obtained of the *monolactone*, $(HO_2C)_2C\cdot CH_2\cdot CH_2\cdot C(OH)\cdot CO_2H$ (O—CO). The silver salt of this substance ($C_8H_8O_9$) was prepared and has the composition $C_8H_6Ag_4O_{10}$. The substance, therefore, readily takes up again the elements of water, as is customary with δ-lactones. It begins to soften at 145°, and at 156° fusion is complete and carbon dioxide is evolved.

On heating an aqueous solution of this lactone in a sealed tube at 150°, the acid is decomposed with elimination of carbon dioxide. If the aqueous solution be evaporated to a small bulk and placed over sulphuric acid, small, star-shaped clusters of crystals gradually appear, and eventually the whole becomes solid. The product is found to have the composition $C_6H_8O_5$, which is that of dihydroxyadipic acid less one molecule of water, and the simplest explanation would be that the substance is the δ-lactone of dihydroxyadipic acid, viz., $CO_2H\cdot CH(O—CO)\cdot CH_2\cdot CH_2\cdot CH(OH)$. But careful examination shows that this is not so, for the silver salt was prepared and found to have the composition $C_6H_6Ag_2O_5$. Further investigation shows that the elimination of water takes place between the two hydroxyl-groups, and that the substance is *tetrahydrofurfuran-aa'-dicarboxylic acid*, formed thus:



This substance begins to melt at 65°, but fusion proceeds only gradually, and is not complete till about 120°. The absence of a definite melting point pointed to it being a mixture of stereoisomeric acids, and experiments were made to separate them by fractional crystallisation from water.

A higher melting *tetrahydrofurfuran-aa'-dicarboxylic acid* ($C_6H_8O_5$), m. p. 123—125°, was isolated, and also crystals melting at 63—64°, which had the composition $C_6H_{10}O_6$. This latter substance was at first supposed to be dihydroxyadipic acid, but the silver salt was prepared and found to be $C_6H_6Ag_2O_5$, a result which led to the conclusion that the substance was the isomeric *monohydrate of tetrahydrofurfurandicarboxylic acid.*

When the substance $C_6H_{10}O_6$ (m. p. 63—64°) was placed for some days over strong sulphuric acid, the product melted at 93—95°, and it then had the composition $C_6H_8O_5$. Its silver salt was $C_6H_6Ag_2O_5$, confirming the conclusion that the substance $C_6H_8O_5$(m. p. 93—95°)

was a lower melting *tetrahydrofurfuran-aa' dicarboxylic acid.* It reverts to the monohydrate when exposed in the air.

This case of geometrical isomerism would appear to be the first one established in the furfuran series.

The author also discusses and criticises F. Tiemann's work on isosaccharic acid and "norisosaccharic acid," and shows that all the derivatives of these two acids which he has described are probably derivatives of $\beta\beta'$-dihydroxytetrahydrofurfuran-aa'-dicarboxylic acid.

134. "The application of powerful optically active acids to the resolution of externally compensated basic substances. Resolution of tetrahydroquinaldine." By William Jackson Pope and Stanley John Peachey.

In continuation of previous work (*Proc.*, 1899, 15, 124), the authors find that dextrotetrahydroquinaldine cannot be prepared in quantity in a pure condition from the dextrocamphorsulphonate nor the hydrochloride of the crude dextro-base obtained from the inactive base; the benzoyl-derivative of the dextro-base can be easily isolated from the crude dextro-base, and on hydrolysis with hydrochloric acid yields the dextro-base in a pure state.

The following molecular rotations, determined in dilute aqueous solution, are closely related in that the values for the first two salts can be calculated directly from those of the third and fourth:—

Dextrotetrahydroquinaldine dextrocamphorsulphonate ...	$[M]_D = +173{\cdot}3°$
Lævo " " " " ...	$[M]_D = -69{\cdot}5$
" " " hydrochloride	$[M]_D = -121{\cdot}7$
Ammonium dextrocamphorsulphonate	$[M]_D = +51{\cdot}7$

135. "The application of powerful optically active acids to the resolution of feebly basic substances. Resolution of camphoroxime." By William Jackson Pope.

The only basic substances hitherto resolved into optically active compounds by crystallisation with an optically active acid have been powerful bases, because feeble bases do not form stable salts with tartaric acid. By using a powerful optically active acid, however, feebly basic externally compensated substances, such as oximes, may be resolved. Thus by fractionally crystallising a mixture of racemic camphoroxime with Reychler's dextrocamphorsulphonic acid from a solution in acetone or ether, the isomeric salts, *dextrocamphoroxime dextrocamphorsulphonate* and *lævocamphoroxime dextrocamphorsulphonate*, $C_{10}H_{16}NOH,C_{10}H_{15}OSO_3H,H_2O$, may be isolated; the former

has the specific rotation $[\alpha]_D = +4{\cdot}3°$, whilst the latter gives $[\alpha]_D = +41{\cdot}7°$. Both salts are decomposed by water, yielding the corresponding optically active camphoroximes.

136. "The application of powerful optically active acids to the resolution of externally compensated basic substances. Resolution of tetrahydroparatoluquinaldine." By William Jackson Pope and Edmund Milton Rich.

In continuation of previous work (*Proc.*, 1899, **15**, 171), the authors have isolated *dextrotetrahydroparatoluquinaldine* as its hydrochloride from the mother liquors remaining after separating the lævo-isomeride as dextrobromocamphorsulphonate from the externally compensated base; the *hydrochloride* of the new base crystallises in sphenoidally hemihedral orthorhombic crystals containing one molecule of water. The optically active bases themselves crystallise from light petroleum solutions in hemimorphic, monosymmetric prisms.

137. "Homogeneity of dextrolævo-α-phenethylamine dextrocamphorsulphonate." By William Jackson Pope and Alfred William Harvey.

Externally compensated α-phenethylamine combines with Reychler's dextrocamphorsulphonic acid, yielding *dextrolævo-α-phenethylamine dextrocamphorsulphonate*, $CH_3{\cdot}CH(Ph){\cdot}NH_2,C_{10}H_{15}OSO_3H$, which crystallises from acetone in minute, colourless prisms melting at 141—143°. The salt has the molecular rotation $[M]_D = +51{\cdot}5°$ in dilute aqueous solution, and since ammonium dextrocamphorsulphonate gives $[M]_D = +51{\cdot}7°$ in aqueous solution, the new salt belongs to the class of partially racemic substances discovered by Ladenburg. Externally compensated *α-phenethylamine platinochloride*, $(CH_3{\cdot}CHPh{\cdot}NH_2)_2,H_2PtCl_6$, crystallises in golden-yellow scales melting at 213—214°.

138. "The characterisation of racemic liquids." By Frederic Stanley Kipping and William Jackson Pope.

It is shown that the results obtained by Ladenburg's latest method (*Ber.*, 1899, **32**, 1822) for discriminating between "racemic" and "non-racemic" liquids have no bearing upon the question they are supposed to answer.

Series of experiments have further been made to determine the equilibrium between mixtures of dextro- and lævo-pinene in various proportions and their solutions in ethyl and methyl alcohol. It is shown that the distribution ratio of the excess of one antipodes over

the other in the oil and in the alcoholic solution in contact with it is nearly independent of the concentration of that excess. This behaviour is explained by Nernst's distribution law, and would be expected with both racemic and non-racemic substances.

Experiments with dextro- and lævo-camphorsulphonic chlorides are also described, which show the fallacious nature of the conclusions drawn by the application of Ladenburg's method.

139. "A method for discriminating between 'non-racemic' and 'racemic' liquids." By William Jackson Pope and Stanley John Peachey.

The densities of lævo- and externally compensated tetrahydroquinaldine are the same under similar conditions, namely, $d_{t/4°} = 1{\cdot}01930 + 0{\cdot}00079\ (20 - t)$ between 14° and 21°; their molecular refractions are also the same, the observed values being $\mathfrak{M}_D = 47{\cdot}50$ for the active, and $\mathfrak{M}_D = 47{\cdot}57$ for the inactive base. These numbers afford no evidence that the inactive liquid base is racemic.

The variations in specific rotation of non-electrolytes dissolved in various solvents are traced, in the main, to variations in the association factor of the dissolved substance, and it is shown that the highly associated lævotetrahydroquinaldine has specific rotations varying from $[\alpha]_D = -46°$ to $-118°$ in different solvents. On dissolving the base in solvents having nearly its own association factor, such as tetrahydroquinoline, the specific rotation of the active base remains nearly the same as in the solvent-free state, because its association factor remains nearly unchanged; lævotetrahydroquinaldine, when dissolved in the externally compensated base as solvent, has practically the same specific rotation as in the pure liquid state, namely, $[\alpha]_D = -58{\cdot}12°$. It follows that externally compensated tetrahydroquinaldine has the same molecular weight in the liquid state as its active components, and consequently cannot be a racemic compound.

It is shown that the specific rotation of lævopinene, an unassociated liquid, changes comparatively slightly with the solvent, and that it has the same specific rotation when dissolved in the externally compensated hydrocarbon as when in the pure liquid state. Inactive pinene is therefore not racemic.

The authors conclude that the above results afford the first method for discriminating between racemic and non-racemic liquids which has yielded positive results.

140. "On two hydrated cobalt oxides, green- and buff-coloured." By W. N. Hartley, F.R.S.

The preparation and analysis of two hydrated cobalt oxides is described. The green compound was formed when a cold solution of cobalt chloride was precipitated by an equivalent quantity of barium hydroxide, both solutions having been boiled, and a Torricellian vacuum being maintained in the precipitating vessels. Its formula is $Co_3O_4,6H_2O$. The buff-coloured compound resulted when the precipitation was carried out in like manner, but with excess of barium hydroxide. Its composition is $Co_8O_9,11H_2O$.

The action of acetic acid on the green hydrate separates a brown oxide already known as Co_3O_4. There was a similar action and the separation of black oxide from the buff-coloured hydrate. This points to the following formulæ: Green hydrate, $Co_2O_3,Co(OH)_2,5H_2O$. Buff hydrate, $Co_2O_3,6Co(OH)_2,5H_2O$. These are distinct compounds, and not merely mixtures.

141. "A method of separating isomeric xylidenes from the commercial product." By W. R. Hodgkinson and L. Limpach.

This method depends on the fact that acetate of meta-(Me : Me : NH_2 = 1 : 3 : 4)-xylidine crystallises very readily when the crude mixture is treated with acetic acid. From the filtrate from this acetate, hydrogen chloride precipitates the para-(Me : NH_2 : Me = 1 : 2 : 4)-xylidine as hydrochloride, and the filtrate from this, on concentration and heating, yields up the hydrochloride of the (Me : NH_2 : Me = 1 : 2 : 3)-xylidine as a crystalline sublimate. The residue of hydrochlorides of the two ortho-(Me : Me : NH_2 = 1 : 2 : 3 and Me : Me : NH_2 = 1 : 2 : 4)-xylidines is hydrolysed and the bases converted into formyl derivatives; that from the (Me : Me : NH_2 = 1 : 2 : 3)-base crystallises moderately easily, whilst the other from the (Me : Me : NH_2 = 1 : 2 : 4) base is exceedingly difficult to obtain as a solid.

142. "Action of hydrolytic agents on α-dibromocamphor, and the constitution of bromocamphorenic acid." By Arthur Lapworth.

In addition to the experiments already briefly described (*Proc.*, 1899, 15, 161), the paper gives an account of the behaviour of α-dibromocamphor towards hydrolytic agents other than moist silver compounds. It is found that this substance is readily attacked by mercurous nitrate dissolved in boiling acetic acid, and that a small quantity of bromocamphorenic acid is obtained. It is not attacked by lead compounds under these conditions, and chars when heated

with water and lead oxide in closed tubes to 120—150°; in the latter case, no bromocamphorenic acid could be detected, but a small quantity of camphoric acid, and in one instance a minute quantity of camphorquinone, was found to be produced.

The action of oxidising agents on dibromocampholid, bromocamphorenic acid, α-monobromocampholid and other derivatives of camphorenic acid has been investigated. It is found that in each case where oxidation occurs nearly pure homocamphoronic acid is obtained, an excellent yield of the latter substance being produced when α-monobromocampholid is oxidised with dilute nitric acid and silver nitrate.

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Dymond, T. S. Report on the visit of Essex agriculturists to Holland, May and June, 1899. Chelmsford 1899.

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—— ——. Liquid ammonia as a solvent. (*American Chemical Journal*, vol. xx., 1899.)

At the next meeting on Thursday, November 16th, the following papers will be read :—

"Chlorine derivatives of pyridine. Part IV. Constitution of the tetrachlorpyridines." By W. J. Sell, M.A., and F. W. Dootson, M.A.

"Contributions to our knowledge of the aconite alkaloids. Part XV. On Japaconitine and the alkaloids of Japanese aconite." By Wyndham R. Dunstan, F.R.S., and Harold M. Read.

"On the determination of transition temperatures." By H. M. Dawson, Ph.D., B.Sc., and P. Williams, B.Sc.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 15. No. 214.

November 16th, 1899. Professor Thorpe, F.R.S., President, in the Chair.

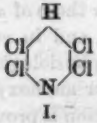
Certificates were read for the first time in favour of Messrs. Herbert William Hart, 13 Lynwood Villas, Darwen, Lancashire; Henry William Hutchin, Basset Road, Camborne.

The following Certificate was authorised by Council: Frank J. Pye, Towrang, New South Wales, Australia.

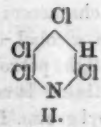
Of the following papers, those marked * were read.

***143. "The chlorine derivatives of pyridine. Part IV. The constitution of the tetrachloropyridines." By W. J. Sell, M.A., F.I.C., and F. W. Dootson, M.A.**

The three theoretically possible tetrachloropyridines have all been obtained (*Trans.*, 1898, 73, 432), and are represented by the formulæ I, II, and III respectively.



I.



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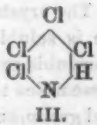
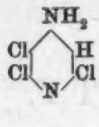


III.

Having already proved (*Trans.*, 1897, 71, 1081) that the compound melting at 90—91° has the constitution represented by formula I, the authors show in the present paper that the isomer which melts at 21—22° is represented by formula III, and hence formula II must represent the constitution of the third isomer, which melts at 74—75°. Treatment with ammonia converts the compound melting

at 21—22° into an aminotrichloropyridine, which is quite different from that described by Stokes and Pechmann (*Amer. Chem. Jour.*, 1886, **6**, 377), and shown by them to have either the formula IV or possibly IVA; as the new compound contains an amino-group in the γ-position, it must be represented by formula V.



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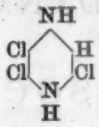
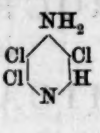
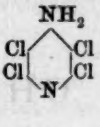


IVA.



V.



VI.

That the γ-position is occupied by the amino-group is evident from the fact that when this new compound is heated with phosphorus pentachloride, the aminotetrachloropyridine obtained is that which has been shown by Stokes and Pechmann, and by the authors, to have the constitution represented by formula VI.

***144. "Contributions to our knowledge of the aconite alkaloids. Part XV. On japaconitine and the alkaloids of Japanese aconite." By Wyndham R. Dunstan, F.R.S., and Harold M. Read.**

The authors have investigated the properties of the alkaloids of Japanese aconite, *A. Fischeri* ("kuza uzu"), including those of japaconitine, the crystalline toxic alkaloid examined by Wright and Luff in 1879, who assigned to it the formula $C_{66}H_{88}N_2O_{21}$. Later workers, Mandelin, Lübbe and, more recently, Freund and Beck, have asserted that japaconitine is identical with aconitine, the crystalline toxic alkaloid of *Aconitum Napellus*.

The results obtained in the present investigation do not confirm these statements, but lead to the conclusion that japaconitine is a distinct alkaloid, the composition and properties of which, however, do not agree with those ascribed to it by Wright and Luff.

Japaconitine crystallises in colourless needles which melt at 204·5° (corr.). The crystallographic characters differ from those of aconitine. The base is soluble in acetone, alcohol, chloroform, and in ether, but almost insoluble in water and light petroleum. Its physiological action closely resembles that of aconitine. It contains four methoxyl groups, one acetyl group, and one benzoyl group. Its composition is provisionally represented by the formula $C_{21}H_{29}(OCH_3)_4(CH_3CO)(C_6H_5CO)NO_2$, which seems to agree best with the analytical data for the base and its derivatives. Japaconitine furnishes a series of well crystallised salts, of which the *hydrochloride* (m. p. 149—150°), the *hydrobromide* (m. p. 172—173°), the *hydriodide* (m. p. 207—208°), the *aurichloride* (m. p. 231°), and the *nitrate* (m. p. 194°) are described. Like aconitine,

japaconitine is dextrorotatory, the salts being lævorotatory. The specific rotation of japaconitine is, however, much greater than that of aconitine.

When partially hydrolysed by dilute acids, japaconitine furnishes acetic acid, and a new crystalline base, *japbenzaconine*, in accordance with the equation $C_{34}H_{49}NO_{11} + H_2O = C_{32}H_{47}NO_{10} + C_2H_4O_2$. It crystallises in rectangular plates which melt at 182—183°. Its lævorotation is nearly twice that of benzaconine. The salts crystallise with extreme readiness. The *hydrochloride* (m. p. 253°), the *hydrobromide* (m. p. 205°), the *aurichlorids* (m. p. 228°), and the colourless *aurichlor*-derivative (m. p. 178°) are described.

Japbenzaconine is hydrolysed on treatment with acids or alkalis, yielding benzoic acid and a base, *japaconine*, in accordance with the equation $C_{32}H_{47}NO_{10} + H_2O = C_{25}H_{43}NO_9 + C_7H_6O_2$. Japaconine has been obtained only in an amorphous condition, even the salts crystallise with great difficulty. The *hydrobromide* melts at 221°.

When japaconitine melts, it gradually suffers decomposition into acetic acid, and a new crystalline base, *pyrojapaconitine*, $C_{32}H_{45}NO_9$. The crystalline *hydrochloride* (m. p. 175—176°), *hydrobromide* (m. p. 208°, or in another form at 241°), and *aurichloride* (m. p. 161°) are described. Both pyrojapaconitine and its salts are strongly lævorotatory.

Pyrojapaconitine is readily hydrolysed by alkalis or acids, yielding *benzoic acid* and *pyrojapaconine*, $C_{25}H_{41}NO_8$. Neither the base nor its salts have been crystallised.

Japaconitine yields a *triacetyl* derivative; and also a *monomethyl* derivative by decomposition of the *methiodide* with potash.

It is evident that the properties of japaconitine and its derivatives are distinct from those of aconitine and its derivatives, although there is a strong general resemblance between the two groups.

Besides the crystalline japaconitine, Japanese aconite roots were found to contain a small proportion of its first hydrolytic product, japbenzaconine.

Discussion.

Professor Tilden inquired how many aconitines were known possessing the physiological action of the original alkaloid from *Aconitum Napellus*, and pointed out the remarkable change in properties resulting from the elimination of the acetyl group from aconitine.

Mr. D. Howard said that it would be of extreme interest if any light could be thrown upon the relation of the chemical constitution of the aconite alkaloids to their physiological action, the problem being of the highest importance.

Professor DUNSTAN, in reply, stated that aconitine from *A. Napellus*, pseudaconitine from *A. ferox*, and japaconitine from Japanese aconite (probably *A. Fischeri*) exerted a very similar physiological action. The relationship between the chemical constitution and the physiological action of these alkaloids and their derivatives was being investigated by Professor Cash and himself. They had already published (*Phil. Trans.*, 1898, 190, B, 239) an account of the work as far as it related to aconitine, benzaconine, and aconine, and had paid special attention to the almost entire loss of toxic power which results from the elimination of the acetyl group from aconitine. In fact, benzaconine and aconine, especially the latter, were found to be, in certain respects, physiologically antagonistic to aconitine.

***145. "The dissociation constants of very weak acids." By James Walker and William Cormack.**

A form of apparatus is described which enabled the authors to measure the electric conductivity of very weak acids with considerable accuracy, the method of experiment adopted being especially applicable to such acids as are gaseous under ordinary conditions.

The following table contains the chief results obtained, hydrochloric and acetic acids being added for purposes of comparison. The first column of figures gives the dissociation constants calculated by Ostwald's formula, the second column gives the percentage degrees of dissociation in decinormal solution, these numbers being proportional to the avidities of the acids.

	$k \times 10^{10}$	100 m.
Hydrochloric acid	—	91·4
Acetic acid	180,000	1·30
Carbonic acid	3,040	0·174
Hydrogen sulphide	570	0·075
Boric acid	17	0·013
Hydrocyanic acid	13	0·011
Phenol.....	1·3	0·0037

These results are in general harmony with the hydrolytic experiments of Shields.

DISCUSSION.

Mr. L. M. JONES asked whether the weak inorganic acids examined obeyed Ostwald's dilution law, as considerable differences occur with strong inorganic acids, and whether the dissociation in all cases proceeded with the formation of only the monovalent anion.

Mr. VERNON HARCOURT hoped that the actual measurements of the conductivity were given in the paper, and not only the inferences from

these measurements. Careful physical measurements, where all conditions were recorded, had a value more certain to endure than the theory used to interpret them.

Professor TILDEN mentioned that, at his suggestion, one of his students had lately studied the conductivity and hydrolytic effects of azoimide in the expectation of finding it a tolerably strong acid. The results of these experiments, which would shortly be communicated to the Society, however, led to the conclusion that azoimide is a weak acid standing very near to hydrocyanic acid.

Professor WALKER, in reply, said that all the acids investigated obeyed Ostwald's dilution law, and that the primary dissociation in each case was therefore into one atom of hydrogen and the rest of the molecule.

Whether the theory of electrolytic dissociation were finally accepted or rejected in its present form, the "degree of dissociation" would always remain a valuable and, indeed, indispensable magnitude where aqueous solutions of electrolytes were concerned, for by its means alone is it possible to calculate chemical equilibrium in such solutions. The interpretation and the name of the magnitude might be changed, but the magnitude itself is a fundamental one.

***146. "Preparation and properties of solid ammonium cyanate." By James Walker and John K. Wood.**

In a preliminary communication (*Proc.*, 1898, 108), the authors showed that pure solid ammonium cyanate might be prepared by mixing cooled ethereal solutions of ammonia and cyanic acid. The same substance can be produced by mixing ammonia gas and cyanic acid vapour at the ordinary temperature, provided the reacting gases are sufficiently diluted with some indifferent gas.

Measurements of the rate of transformation of the solid cyanate into urea showed that the rapidity of transformation increases very rapidly with rise of temperature, and that the presence of moisture greatly accelerates the action. About 3 per cent. of the cyanate is decomposed, with formation of ammonia.

The molecular heat of transformation of solid cyanate into solid urea is 49K; the molecular heat of formation of solid cyanate is 738K; and the molecular heat of solution in water is −62·3K. From these numbers, it appears that the molecular heat of transformation in aqueous solution is 75K.

Ethylammonium cyanate is rapidly transformed into ethyl-urea at the ordinary temperature. When ethereal solutions of aniline and cyanic acid are mixed, the substance which separates is not phenyl-ammonium cyanate, but phenyl-urea.

***147. "Etherification of derivatives of β-naphthol." By William A. Davis.**

The author has studied quantitatively the etherification of a considerable number of substitution derivatives of β-naphthol by means of alcohol and sulphuric acid. It is shown that a single group occupying position 1 has a most remarkable effect in limiting etherification, although the same group in position 3′ exercises little influence.

The inhibiting influence of ortho-groups on the etherification of phenols, and of substituted benzoic acids, as studied by Victor Meyer and others, is fully discussed; the conclusion arrived at is that the stereochemical hypothesis proposed by V. Meyer to explain his results is not justified by facts.

The following ethers are described: 3′-*bromo-β-methoxynaphthalene*, m. p. 105°; 1-*bromo-β-methoxynaphthalene*, m. p. 82—83°; 1-*chloro-β-methoxynaphthalene*, m. p. 68°; 1 : 3′-*dibromo-β-methoxynaphthalene*, m. p. 100°; 3′-*bromo-β-ethoxynaphthalene*, m. p. 80°; 1-*bromo-β-ethoxynaphthalene*, m. p. 66°; 1-*chloro-β-ethoxynaphthalene*, m. p. 58°; 1 : 3′-*dibromo-β-ethoxynaphthalene*, m. p. 94°; 1 : 3′-*chlorobromo-β-ethoxynaphthalene*, m. p. 77°; 3′-*bromo-β-propoxynaphthalene*, m. p. 63·5°; 1-*bromo-β-propoxynaphthalene*, m. p. 35—36°; 1 : 3′-*dibromo-β-propoxynaphthalene*, m. p. 75°; and 1 : 3′-*chlorobromo-β-propoxynaphthalene*, m. p. 60·5°.

148. "On the determination of transition temperatures." By H. M. Dawson, Ph.D., B.Sc., and P. Williams, B.Sc.

While the influence of temperature on homogeneous and heterogeneous equilibrium is a continuous one, the so-called 'condensed systems' are characterised by the existence of a transition temperature. At this temperature, the system suddenly undergoes a complete change. The second form of the system, which is stable at the higher temperature, is entirely retransformed into the first on lowering the temperature below that of the transition point.

Various methods have been employed for the determination of such transition temperatures, for example, the dilatometric, the thermometric, and the various identity methods. The latter depend upon the fact that the saturated solutions of the systems which are capable of mutual transformation become identical at the transition temperature. In consequence of this, the properties of the saturated solutions corresponding to the various solubility curves emanating from the transition point assume the same value at this temperature. In choosing a suitable property of the saturated solution for investigation, attention must be paid to the three following points: (1) the property in

question must be measurable accurately and rapidly; (2) it must show a notable variation for small changes in the composition of the saturated solution; (3) there should, if possible, be no loss in the quantity of the saturated solution as a result of the measurement.

The densities and electric conductivities of saturated solutions have been investigated by the authors with a view to determining transition temperatures. The density measurements were carried out with the saturated solution of sodium sulphate. The curves obtained by plotting the density intersect at a wide angle at 32·4° corresponding to the transformation of the decahydrate into the anhydrous salt at this temperature.

Conductivity measurements were also carried out with this salt; as in the case of the density, two curves intersecting at about 32·5° were obtained.

The change in direction of the curve at this temperature is not so great as was expected; this is, however, explicable on the ground that the solutions are so concentrated.

A second series of experiments was carried out with thorium sulphate, the nonahydrate of which, according to Roozeboom, changes into the tetrahydrate at about 43°. The concentration of the saturated solution at the transition temperature is, in this case, only about one-third normal.

On plotting the conductivity on a diagram, two curves are obtained intersecting at about 48°. To confirm this result, the transition temperature has been determined dilatometrically and tensimetrically, by which methods 46·5° and 47·5° were obtained. Roozeboom's determination of 43° would therefore appear to be somewhat too low. The authors point out the availability of the above methods of determination in cases where other methods cannot be used with advantage.

149. "Constitution of amarine, of its supposed dialkyl- and diacyl-derivatives, and of isoamarine." By Francis R. Japp, F.R.S., and James Moir, M.A., B.Sc.

The authors find that Claus and Elbs's "dibenzylamarine" (m. p. 139—140°) has in reality the composition represented by the formula $C_{21}H_{18}(C_7H_7)_2N_2O$, and is *benzoyl-s-dibenzyl-i-diphenylethylenediamine*, $C_6H_5\cdot CH\cdot N(C_7H_7)\cdot CO\cdot C_6H_5$. It may be obtained, along with a di-$C_6H_5\cdot CH\cdot NH\cdot C_7H_7$
benzoyl derivative (m. p. 268°), by the action of benzoic chloride on Grossmann's *s*-dibenzyl-*i*-diphenylethylenediamine, thus proving its constitution. This dibenzoyl derivative, melting at 268°, may also be obtained by introducing a benzoyl group into "dibenzylamarine." Claus and Elbs's "dimethylamarine" (m. p. 146°) is in reality

the corresponding *benzoyl-s-dimethyl-i-diphenylethylenediamine*, and Borodine's "diethylamarine" (m. p. 110—115°; the authors find 125°) is the corresponding diethyl derivative.

When benzoyl-*s*-dibenzyl-*i*-diphenylethylenediamine hydrochloride is heated to 220°, it parts with water, yielding dibenzylamaronium chloride,

$$\begin{matrix} C_6H_5\cdot CH\cdot N(C_7H_7)\cdot CO\cdot C_6H_5 \\ C_6H_5\cdot CH\cdot N^{V}(C_7H_7)H_2Cl \end{matrix} = \begin{matrix} C_6H_5\cdot CH \text{——} N(C_7H_7) \\ C_6H_5\cdot CH\cdot N^{V}(C_7H_7)Cl \end{matrix} \!\!>\!\! C\cdot C_6H_5 + H_2O,$$

a reaction which proves conclusively the constitution of the dialkylamaronium salts.

Dibenzylamaronium chloride gives a dichromate of the formula $(C_{35}H_{31}N_2Cl)_2,H_2Cr_2O_7$ (m. p. 173°) which, when boiled with glacial acetic acid and a little hydrochloric acid, yields *dibenzyllophonium chloride*, showing that the latter substance has the constitution

$$\begin{matrix} C_6H_5\cdot C \text{——} N(C_7H_7) \\ \| \qquad\qquad \\ C_6H_5\cdot C\cdot N^{V}(C_7H_7)Cl \end{matrix} \!\!>\!\! C\cdot C_6H_5,$$

instead of, as suggested by Japp and Davidson,

$$\begin{matrix} C_6H_5\cdot C\cdot N^{V}(C_7H_7)_2Cl \\ \| \qquad\qquad\qquad \\ C_6H_5\cdot C \text{————————} N \end{matrix} \!\!>\!\! C\cdot C_6H_5.$$

The authors regard amarine as 2-*phenyl*-4 : 5-cis-*diphenyl*-4 : 5-*dihydro-imidazole*,

$$\begin{matrix} H \\ C_6H_5\cdot \dot{C}\cdot NH \\ | \qquad\quad \\ C_6H_5\cdot \dot{C} \text{——} N \\ H \end{matrix} \!\!>\!\! C\cdot C_6H_5,$$

employing the numbering of the imidazole ring adopted by M. M. Richter. A formula identical with the foregoing, excepting that the configuration was not indicated, was put forward by Claus.

Amarine is thus a meso-form derived from Grossmann's *i*-diphenylethylenediamine (m. p. 120—121°), which this author obtained by the reduction of amarine.

The authors show that Snape and Brooke's isoamarine is 2-*phenyl*-4 : 5-trans-*diphenyl*-4 : 5-*dihydroimidazole*—the corresponding racemic form. With Professor Snape's permission, they reduced isoamarine with sodium in boiling alcohol, and obtained, as in Grossmann's analogous experiment with amarine, a benzylidene derivative, which on hydrolysis with acids, gave benzaldehyde and a base—in this case Feist's *r*-diphenylethylenediamine (m. p. 90—92°). Isoamarine is thus related to Feist's base in the same way as amarine to Grossmann's. Feist's base (prepared by the reduction of α-benzildioxime), when heated with benzoic acid at 170—180°, yielded isoamarine, thus confirming the foregoing view as to the constitution of the latter compound. Amarine benzoate undergoes no change at this temperature.

Isoamarine may be readily prepared by fusing amarine with sodium, or by heating amarine hydrochloride above its melting point.

The authors find that Claus and Scherbel's supposed dibenzoylamarine is identical with Grossmann's *s*-dibenzoyl-*i*-diphenylethylenediamine,

and that Bahrmann's supposed diacetylamarine is acetylbenzoyl-*i*-diphenylethylenediamine. This removes the supposed evidence for the symmetrical or di-imidic formula of amarine.

The authors have made a detailed study of the reactions of the supposed dibenzylamarine, the results of which confirm the foregoing views as to its constitution.

150. "The atomic weight of nitrogen." By G. Dean, B.A.

The work of which an account is given in this paper is in continuation of that of which a preliminary notice has already been communicated to the Society (*Proc.*, 1898, 14, 174). After giving a summary of the results of previous workers, the author deduces a mean value from them of 14·034 for the atomic weight of nitrogen, but points out that the means of the determinations by chemical methods of individual workers vary from 13·975 (Pelouze) to 14·05 (Stas). The ratio of the densities of oxygen and nitrogen as determined by Lord Rayleigh and by M. Leduc is 16 : 14·003. These variations seemed to be too great, so it was thought that it would be both important and interesting to try a new method which would involve as few atomic weights as possible, and only those which are known with the highest accuracy. Silver cyanide was selected as the compound containing nitrogen, and the ratio between a given mass of it and that of the potassium bromide required for the complete precipitation of the silver contained in it determined with all the precautions insisted on in such work by Stas. The cyanide was decomposed in some cases by dissolving it in nitric acid, in other experiments sulphuric acid. The ratio between the purest silver and the sample of potassium bromide used was carefully determined, so that the ratio found was really Ag : AgCN. This was found to be 107·93 : 133·962, whence CN = 26·032 and N = 14·031 if C = 12·001.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

The following Candidates have been proposed for election. A ballot will be held on Thursday, December 7th, 1899.

Anderson, James William,
1, Preston Villas, Halling, Kent.

Analytical Chemist. Student, Rutherford College, Newcastle-on-Tyne, in Chemistry and Metallurgy, &c. Assistant Chemist for 12 years, Messrs. Rio Tinto Co., Limited, at Jarrow-on-Tyne, in the extraction of copper, silver, gold, lead, &c., and smelting and refining of copper, &c. Head Chemist, Messrs. Hilton, Anderson, Brooks and Co., Limited, Cement Manufacturers, 6, Upper Thames Street, London, and elsewhere.

George Thudichum. Robt. G. Grimwood.
W. J. Dibdin. *Leopold Mandeville Deane.*
A. Stanley Fox.

Armitage, Francis Paul,
High House, Brook Green, Hammersmith.

Assistant Science Master at St. Paul's School. First Class Honours in Chemistry at Oxford, 1898.

W. W. Fisher. V. H. Veley.
John Watts. J. E. Marsh.
Wyndham R. Dunstan.

Armstrong, Frederick William,
The Hill, Langport, Somerset.

Science Master and Evening Lecturer. Past Royal Exhibitioner at the Royal College of Science. Associate of the Royal School of Mines.

T. E. Thorpe. W. Palmer Wynne.
F. R. Japp. A. E. Tutton.
T. H. Walker.

Beesley, Frederic Arnold,

Bank House, Wirksworth, Derby.

Lecturer and Teacher of Chemistry and Physics at the Ashby-de-la-Zouch Grammar School. For 5 years I was a student of Chemistry at University College, Nottingham, where I carried on my work considerably beyond the standard of the London B.Sc. I hold this degree in Chemistry and in Physics with Honours. I have been teaching Chemistry (Theoretical and Practical) for the past two years.

Frank Clowes.	J. J. Sudborough.
J. Bernard Coleman.	R. M. Caven.
R. Lloyd Whiteley.	*E. T. Shelbourn.*

Chapman, Edgar Marsh,

17, Bloomsbury Square, London, W.C.

Holder of the Burroughs Scholarship in the Pharmaceutical Society's Laboratory. Have studied Chemistry for two years under Professor J. Norman Collie, and passed the Pharmaceutical Society's examination; have been engaged for a year in Research work; joint author of paper on "Homocamphoronic and Camphononic Acids," *Proc.*, 1899, 15, 159.

J. Norman Collie.	M. Carteighe.
A. Lapworth.	Thomas Tickle.

John E. Mackenzie.

Dewhirst, John Arthur,

125, Mount View Road, Stroud Green, N.

Chemist. Studied at Bradford Technical College, Yorkshire College, Leeds, and at Pharmaceutical Society's School. Three times Medallist at latter institution. Formerly Assistant in Laboratory of Dr. Attfield, F.R.S. Latterly Demonstrator of Chemistry, School of Pharmaceutical Society. Now Chemist to Messrs. Geo. Curling, Wyman and Co., Bunhill Row.

John Norman Collie.	Wyndham R. Dunstan.
Arthur Lapworth.	Arthur Smithells.

Wm. Ackroyd.

Dougall, James Dick,

Millom, Cumberland.

Analytical Chemist. Was three years a Student and two years an Assistant with Messrs. Tatlock and Thomson, of Glasgow. Since then have been head Chemist in large works in Cumberland, and have contributed one or two small papers to the *Analyst* and local societies in Glasgow.

R. R. Tatlock.	Horatio Ballantyne.
R. T. Thomson.	*John Clark.*
W. Rintoul.	*Wm. T. Thomson.*

Dudderidge, Frank Rawlinson,

45, Sidney Grove, Newcastle-on-Tyne.

Analytical and Pharmaceutical Chemist. **Principal of the North of England School of Chemistry, 55, Northumberland Street, Newcastle-on-Tyne, where I lecture on Chemistry daily. Medallist in Chemistry at the South London School of Chemistry (1890—91). For some time Analytical Chemist with Messrs. Brady and Martin, Manufacturing Chemists, Newcastle-on-Tyne.**

P. Phillips Bedson. Geo. F. Merson.
Fredk. Gilderdale. *W. A. H. Naylor.*
Thomas Tyrer.

Fermor, Herbert Frederick Francis Burdett,

15, Ansdell Road, Peckham, London, S.E.

Analytical Chemist. **Mainly educated in Science by private study. Student at Goldsmiths' Institute, then Demonstrator in the Chemical Department at the same institution. Lecturer on Chemistry to London School Board. Assistant Analyst, Chemical and Gas Department, London County Council. Medallist in Chemistry, Science and Art Department.**

Frank Clowes. R. Grimwood.
William Jackson Pope. J. H. Coste.
A. G. Bloxam. Charles J. S. Makin.

Gurney, Elliott Henry,

Albert Street, Marrickville, New South Wales.

Assistant Chemist, Department of Agriculture, New South Wales. **Seven years assistant to Mr. F. B. Guthrie, Chemist to Department of Agriculture, N.S.W. Author of "Notes on Colouring Matter of *Eriococcus Eucalypti*," and "The Wax of *Ceroplastes Rubens*," (published in Vol. VII. *Australian Association for Advancement of Science*). Also, with Mr. Guthrie, "Notes on Milling Qualities of Different Varieties of Wheat," and "Analyses of Commercial Fertilisers obtainable in N.S.W.," and of other papers in the *Agricultural Gazette*, N.S.W.**

William M. Hamlet. H. G. Smith.
F. B. Guthrie. W. M. Doherty.
A. Liversidge. J. A. Schofield.
Will. A. Dixon.

Kay, Percy,

3, Phene Street, Chelsea, S.W.

Senior Demonstrator, S.W. London Polytechnic, Chelsea. **Ph.D. in Chemistry of Heidelberg. Fellow of the Institute of Chemistry.**

Author of the following papers: "Action of Mustard oils on aromatic acids diacetanilides," "Urethane derivatives and nitro-piperidine."

J. Bernard Coleman. R. Grimwood.
Frank Clowes. *J. H. Coste.*

A. Hunter Boylan.

Kinnersley, Henry Wulff,

4, The Avenue, Keynsham, Somerset.

Student. One year Merchant Venturers' Tech. College, Bristol. Three years Dr. E. H. Cook, Bristol. One year King's College, London. Passed Intermediate Examination of the Institute of Chemistry. Passed Honours Examination in Chemistry of Science and Art.

John M. Thomson. Patrick H. Kirkaldy.
Herbert Jackson. Martin Priest.

Ernest H. Cook.

Lange, Ernest Frederick Stephen,

Sunny Nook, Victoria Road, Withington, Manchester.

Steel Works Manager, *i.e.*, Metallurgical Engineer. Practical and Theoretical Research into the Metallurgy of the melting of steel in the Siemens Open Hearth Furnace, the Metallurgy of the various small converter processes for making steel, the mixing of special foundry irons, desulphurisation by means of ferromanganese, &c., &c.

J. E. Stead. Hugh Ramage.
J. Reddrop. *W. N. Hartley.*

H. Frankland.

Leeming, William Thomas,

60, Lomeshaye Road, Nelson.

Science Teacher. Student of Owens College, 1892—1895, in the Honours School of Chemistry, and B.Sc. (Vict. Univ.). Science Master in the Nelson Technical School, and Lecturer in Chemistry in the Nelson Evening School.

H. B. Dixon. W. H. Perkin, jun.
G. H. Bailey. *J. F. Thorpe.*
W. A. Bone. *W. T. Lawrence.*

Lett, Stephen Joshua,

(In England), 25, Percy Street, Liverpool.

Assayer and Technical Chemist. Sole charge of Assay Office in Central Africa of Messrs. The North Charterland Exploration Co., Ltd., for past two years (this position I still hold). Sole charge of Assay and Chemical Department of Messrs. The Ripanji Quicksilver

and Silver Mines, Ltd., Ripanji, Servia. Analyst for four years to the Gas and Water Committees of Messrs. The Wallasey Local Board (Cheshire, England). Four years Student Assistant to the late Mr. A. Norman Tate, F.I.C., F.C.S.

Francis Henry Tate. T. A. Reid.
William J. Butcher. *Edward Davies.*
F. E. Bowman.

Lewis, Edward Watkin,
64, Ommaney Road, New Cross, S.E.

Student. Associate of the City and Guilds Institute in the Department of Chemistry. Now Salters' Research Fellow at the Central Technical College.

Henry E. Armstrong. William A. Davis.
T. M. Lowry. Edwin C. Jee.
Gerald T. Moody.

McCreath, William D.,
The Plains, Totnes, S. Devon.

Analytical and Technical Chemist. Studied Chemistry first under Dr. C. M. Aikman, of Glasgow. Afterwards assistant for 4½ years to Mr. F. J. Lloyd, during which made a speciality of cider fermentation, assisting Mr. Lloyd in his experiments on cider, and also, during two seasons, in those on cheddar cheese. Now Chemist and Scientific Adviser to Messrs. J. Symons & Co., Cider and Wine Makers, of Totnes.

C. M. Aikman. Alexander Cameron.
Fredk. J. Lloyd. Jas. McCreath.
John Heron. *E. R. Moritz.*
C. H. Bothamley.

Main, Hugh,
45, The Village, Old Charlton, Kent.

Technical Chemist. B.Sc. (Lond.). Seventeen years Chemist at Messrs. H. Tate & Sons, Ltd., Sugar Refiners, London.

Rudolph Messel. Arthur R. Ling.
D. Bendix. Albert Harrison.
B. E. R. Newlands. *Otto Hehner.*

Neale, Harry Ainley,
Brentwood, Clothorn Road, Didsbury, Manchester.

Assistant Chemist in dye-works. Studied Chemistry for four years

at Owens College, Manchester. One year's research with Dr. J. F. Thorpe (work not yet published).

H. B. Dixon. G. H. Bailey.
A. William Gilbody. J. F. Thorpe.
W. H. Perkin, jun.

Palmer, Thomas Henry,

"Amalfi," Longueville, Sydney, N. S. Wales.

Mining and Metallurgical Engineer. 1896—1897, Analytical Chemist to Royal Commission on Coal Cargoes, Sydney. 1898, Graduated for the Degree of Bachelor of Engineering in Mining and Metallurgy, University of Sydney. 1898, Manager of Gold Extraction Cyanide Works, Peak Hill, N.S. Wales. 1899 and at present, General Manager, Overflow Silver Mine and Metallurgical Works, Bobadah, New South Wales. Author of paper on "The Cyanide Process for the Extraction of Gold," and read before the Sydney University Engineering Society, 11th May, 1898.

A. Liversidge. C. Walker.
J. A. Schofield. *F. B. Guthrie.*
William M. Hamlet.

Pearson, Marchant,

The Grammar School, Bridlington.

Schoolmaster. B.A. (Lond. Univ.), Intermediate B.Sc. (Lond. Univ.) Assist. Science Master for four years, 1895—1899, at the Bradford Grammar School (work chiefly Chemistry); joint author of a school manual on Volc. Analysis.

Arthur Thornton. Julius B. Cohen.
Arthur Smithells. J. Maudsley.
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B.Sc. Science Master Alleyn's School, Dulwich College; Demonstrator in Chemistry, Battersea Polytechnic; studied Chemistry as a special branch for Science Degree; is principally engaged in teaching Chemistry as above; was also teacher of Chemistry at Tottenham Polytechnic; holds several Certificates, including Honours, Practical Chemistry, from Science and Art Department.

J. H. Robins. John Wilson.
Thos. J. Cheater. *W. W. S. Nicholls.*
C. H. Burgs.

Ponthieu, Georges,

Pharmacie Centrale de France, Avenue de Paris, St. Denis (Seine).

Manufacturing Chemist. Was three years in the Analytical Laboratory and Manufacturing Department of Messrs. Burgoyne, Burbridge and Co., London. Is, and has been for over two years, Scientific Manager of the Chemical Department at the St. Denis Works of the "Pharmacie Centrale de France" (near Paris).

Thos. Farries. F. M. Mercer.
Theophilus Pitt. *H. Wilson Hake.*
Isaac S. Scarf.

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13, Christ Church Road, Doncaster.

Senior Science Master in the Doncaster Grammar School. B.A. of Hertford College, Oxford, in Natural Science (Chemistry), Honours, 1896. Science Master of the County School, Pembroke Dock, 1896—1898. From September, 1898, to July, 1899, Chemistry Master in the Bradford Grammar School; now Senior Science Master of Doncaster Grammar School.

V. H. Veley. J. E. Marsh.
John Watts. W. W. Fisher.
Arthur Thornton.

Roundell, Christopher Foulis,

Guards' Club, Pall Mall, S.W.

2nd Lieutenant, Coldstream Guards. B.A., Balliol College, Oxford, with Honours in Chemistry.

A. Vernon Harcourt. John Conroy.
Wyndham R. Dunstan. William E. Moss.
D. H. Nagel.

Russell, William,

Thetford, Norfolk.

Analytical Chemist to Matthew's Kentish White Lead Co., East Greenwich. Three years course at the Royal College of Science, S. Kensington. Science Master (Chemistry) at the Grammar School, Wirksworth. At present Chemist to Matthew's Kentish White Lead Co., Morden Wharf, East Greenwich.

William A. Tilden Cecil J. Brooks.
G. Cuthbertson. Chapman Jones.
Francis Sutton.

Walton, Robert Hawks,

424, Park Road, Moore Park, Sydney.

Analyst and Assayer. Chief Assistant to Dr. Helms, 8, Bridge Street. I have been with Dr. Helms for more than 9 years.

A. Helms.	W. M. Doherty.
William M. Hamlet.	John C. H. Mingaye.

Will. A. Dixon.

Wilson, F. R. Leyland,

Charterhouse, Godalming.

Science Master, Charterhouse. M.A., Oxford. Honours in Final Nat. Science School (Chemistry), 1892. Late Assistant-Master at Dulwich College. Chemistry Master at Charterhouse. Worked under Professor Wislicenus at Leipzig on derivatives of diketohydrindene, results not yet published.

H. Brereton Baker.	John Watts.
W. W. Fisher.	A. Hartridge.
V. H. Veley.	J. E. Marsh.

Wilson, John,

73, Melford Road, Leytonstone, E.

Analytical Chemist. Studied at Robert Gordon's College, Aberdeen; at Heriot-Watt College, Edinburgh; under Professor W. H. Perkin, jun., F.R.S., and Professor F. Stanley Kipping, F.R.S.; and at Finsbury Technical College, under J. Castell-Evans, Esq., F.I.C., F.W. Streatfeild, Esq., F.I.C., and Professor Meldola, F.R.S. Eight years' experience in analysis of oils and fats, soaps, glycerine, and essential oils. Engaged on the staff of the Vinolia Company, Ltd.

Henry Garnett.	Herbert E. Burgess.
W. W. Houlder.	R. Meldola.
F. Mollwo Perkin.	*Peter MacEwan.*
A. Jamieson Walker.	*J. T. Hewitt.*

Harold Senier.

The following Certificate was authorised by Council under Bye-law I. (3).

Pye, Frank J.,

Towrang, New South Wales, Australia.

Managing Chemist to the Towrang Acid Works, N.S.W. Four years Assistant Chemist at the Chemical Works of Messrs. Burt, Boulton and Haywood, London. Four years Chemist at Messrs.

Brotherton and Co.'s Tar Works, Leeds. Five years Chemist and Works Manager at the Tar and Ammonia Works of T. H. Harvey, Esq., Plymouth.

Arthur W. Cooke. Harry W. Dixon.
Robert Hamilton. E. G. McBretney.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in December. Applications for Grants, to be made on forms which can be obtained on application to the Assistant Secretary, must be received on or before November 30th.

At the next meeting on Thursday, December 7th, there will be a ballot for the election of Fellows, and the following paper will be communicated by the authors:—

"The oxidation of certain organic acids in presence of iron." By H. J. H. Fenton, M.A., F.R.S., and H. O. Jones, B.A., B.Sc.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 15. No. 215.

December 7th, 1899. Professor Thorpe, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Alexander Hutcheon Bennett, 61 London Road, Bromley, Kent; Oscar Joseph Cole, Wivenhoe, Colchester, Essex; Thomas Cuthbert Davison, 49 Victoria Road, New Swindon, Wilts.; Harry Medforth Dawson, Yorkshire College, Leeds; Stephen M. Dixon, University, Fredericton, New Brunswick, Canada; James Foulds, 5 Murray Street, Burnley, Lancashire; Robert W. Gray, 7 Orme Court, Bayswater; Henry Jackson, Downing College, Cambridge; Thomas Goode Joyce, The Smallthorns, Stafford; William Charles Robert Kynaston, 9 Harland Road, Higher Tranmere, Birkenhead; Arthur Robert Laws, 48 Waverley Terrace, Newcastle-on-Tyne; Alan W. Cranbook Menzies, 11 Howe Street, Edinburgh; Edgar Ford Morris, 69 Shrewsbury Street, Old Trafford, Manchester; Herbert Newall Morris, 48 Lansdowne Road, Crumpsall, Manchester; Ernest Brooks Naylor, 73 Castle Street, Bolton; James Hart-Smith, 4 Edenvale Street, Fulham; Bertram Vincent Storr, 17 York Road, Ilford, Essex; Archie Hugh Strong, Stoneleigh Villa, 63 Herne Hill Road, Camberwell, S.E.; Gustavus Athol Waterhouse, "Ellerslie," Birrell Street, Waverley, N.S.W.; Leonard Philip Wilson, 123 Chadwick Road, East Dulwich, S.E.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Messrs. James William Anderson; Francis Paul Armitage; Frederick William Armstrong; Frederic Arnold Beesley, B.Sc.; Edgar Marsh Chapman; John Arthur Dewhirst; James Dick Dougall; Frank Rawlinson Dudderidge; H. F. F. Burdett Fermor; Elliott Henry Gurney; Percy Kay, Ph.D.; Henry Wulff Kinnersley; Ernest F. Stephen Lange;

William Thomas Leeming, B.Sc.; Stephen Joshua Lett; Edward Watkin Lewis; William D. McCreath; Hugh Main, B.Sc.; Harry Ainley Neale; Thomas Henry Palmer; Marchant Pearson, B.A.; Bennett C. Polkinghorne, B.Sc.; Georges Ponthieu; Frank J. Pye; William Downing Raynor, B.A.; Christopher Foulis Roundell, B.A.; William Russell; Robert Hawks Walton; F. R. Leyland Wilson, M.A.; John Wilson.

Of the following papers, those marked * were read.

*151. "The oxidation of certain organic acids in presence of ferrous salts." By Henry J. Horstman Fenton, M.A., F.R.S., and H. O. Jones, B.A., B.Sc.

The oxidation of various organic substances in presence of iron has formed the subject of a considerable number of previous communications, and the observations are now being extended in several directions. The present paper deals with results which have recently been obtained in an extensive study of the behaviour of acids of typical constitution when oxidised by hydrogen peroxide in presence of ferrous salts.

It is shown that, under the conditions of the experiments, the following acids are unacted upon by the reagent: acetic, monochloracetic, oxalic, malonic, succinic, dibromosuccinic, fumaric, maleic; whereas an energetic, and generally immediate, oxidation occurs in the case of the following acids: formic, glycollic, lactic, β-oxybutyric, glyceric, tartronic, tartaric, malic, citric, mucic, saccharic, pyruvic, dioxytartaric, acetylene dicarboxylic, acetone dicarboxylic, pyromucic, benzoic, picric.

The oxidation products obtained are often of considerable interest, and changes can be effected which have not been accomplished by any other means. These oxidation products are being examined, and in the present communication an account is given of the progress of the investigation.

*152. "Oxalacetic acid." By Henry J. Horstman Fenton, M.A., F.R.S., and H. O. Jones, B.A., B.Sc.

By the oxidation of malic acid in presence of ferrous salts, the authors obtained a white, crystalline substance having the formula $C_4H_4O_5$, which, on examination, was found to be free oxalacetic acid. The hydrazone crystallises in lustrous prisms, and, when heated with dilute sulphuric acid gives the phenylpyrazoloncarboxylic acid which was obtained by Wislicenus and by Buchner from the ethyl and methyl esters. Further identification is afforded by the formation of the

methyl ester and its hydrazone, by the colour reaction with ferric chloride, and by the formation of pyruvic acid when an aqueous solution of the acid is heated.

***153. "Determination of the constitution of fatty acids. Part II." By Arthur William Crossley and Henry Rondel Le Sueur.**

In continuation of their work (*Trans.*, 1899, **75**, 161), the authors have prepared ethylisopropylacetic acid from ethylisopropylmalonic acid, and have investigated it by their method.

Ethylisopropylmalonic acid crystallises from benzene in glistening needles melting at 131—131·5°; the *ethyl* salt is a colourless liquid boiling at 232—233°.

Ethylisopropylacetic acid, $C_2H_5 \cdot CH(C_3H_7) \cdot COOH$, prepared by the elimination of carbon dioxide from ethylisopropyl malonic acid, is a disagreeable smelling liquid boiling at 203°. The *ethyl* salt is a colourless liquid boiling at 164—165° (765 mm.), and possessing a characteristic smell; the *amide* crystallises from light petroleum in silky needles melting at 134°; the *anilide* separates from light petroleum in clusters of small, glistening needles melting at 114—115°; and the *paratoluidide* forms feathery needles melting at 123°.

Ethyl α-bromethylisopropylacetate is a mobile liquid boiling at 135—136° (59 mm.) possessing a pungent smell somewhat resembling peppermint. When treated with diethylaniline, hydrogen bromide is eliminated in two ways, giving rise to a liquid having a marked odour of peppermint, and boiling at 175—180°. It consists of a mixture of *ethyl dimethylethylacrylate* and *ethyl methylisopropylacrylate*. On saponification, a mixture of the corresponding acids is obtained boiling constantly at 136° (55 mm.).

When this mixture is oxidised, first with potassium permanganate and then potassium dichromate, the products are, as expected, acetone, acetic, propionic, and isobutyric acids; thus proving that two unsaturated ethyl salts are formed by the action of diethylaniline on ethyl α-bromethylisopropylacetate.

Applying these results to the determination of the constitution of the original acid, having the formula $C_7H_{14}O_2$, since acetone is produced on oxidation, the group $(CH_3)_2C{:}$ must be attached to the α-carbon atom in the unsaturated acid, the double bond being produced by elimination of a bromine atom from the α-carbon atom, and a hydrogen atom from an adjacent carbon atom, hence $(CH_3)_2C{:}C \cdot COOH$ represents the grouping of five of the seven carbon atoms. The two remaining carbon atoms must be attached to the α-carbon atom, and as propionic acid was obtained, they must have been present as an ethyl group, therefore the formula of the unsaturated acid is

$CH_3)_2C{:}C(C_2H_5)\cdot CO_2H$, and $(CH_3)_2CH\cdot CH(C_2H_5)\cdot CO_2H$ that of the original fatty acid.

The presence of acetic and isobutyric acids is accounted for by the oxidation of the second unsaturated acid produced, namely, methylisopropylacrylic acid.

***154. "The reaction between sulphuric acid and potassium ferrocyanide." By R. H. Adie, M.A., B.Sc., and K. C. Browning, B.A.**

The authors have made a quantitative investigation of the action of sulphuric acid of concentrations varying from that of H_2SO_4 (98 per cent.) to $H_2SO_4,8H_2O$ on potassium ferrocyanide with the following results.

The salt dissolves in acid of strengths corresponding to H_2SO_4 and H_2SO_4,H_2O, with the formation of potassium sulphate and hydroferrocyanic acid; there is only a slow and incomplete formation of carbon monoxide.

In acid of the strength represented by $H_2SO_4,2H_2O$, the decomposition of the salt results in the formation of carbon monoxide; this reaction accounts for all the cyanogen in the salt.

With more dilute acid of the composition of from $H_2SO_4,4H_2O$ to $H_2SO_4,10H_2O$, the products are hydrocyanic acid and Everitt's salt, $K_2Fe_2Cy_8$. At the latter dilution, all the cyanogen in the salt appears as hydrocyanic acid, while the formation of carbon monoxide practically ceases with acid of $H_2SO_4,4H_2O$ strength.

The authors discuss the mechanism of the reaction (i) through the formation and hydrolysis of hydroferrocyanic acid by means of the dilute sulphuric acid; (ii) through the action of the potassium sulphate first formed on the hydroferrocyanic acid, with the intermediate formation of Everitt's salt. The latter reaction only takes place in fairly concentrated solutions, whilst the former alone occurs with acids more dilute than that represented by $H_2SO_4,10H_2O$. Other conditions influencing the reactions are also fully discussed.

***155. "The sulphates of bismuth." By R. H. Adie, M.A., B.Sc.**

The author has investigated the conditions of formation and limits of existence of the sulphates of bismuth, and has found that from sulphuric acid of any strength between those represented by $H_2SO_4,6H_2O$ and $H_2SO_4,12H_2O$, a basic bismuth sulphate having the formula $5Bi_2O_3,11SO_3,17H_2O$ crystallises out; if between $H_2SO_4,3H_2O$ and $H_2SO_4,5H_2O$, the sulphate may be represented as $Bi_2O_3,4SO_3,7H_2O$, and if the strength be between H_2SO_4,H_2O and $H_4SO_4,2H_2O$, the salt obtained has the composition $Bi_2O_3,4SO_3,3H_2O$. From sulphuric acid

itself, the sulphate which crystallises out at temperatures above 170° has the formula $Bi_2O_3,4SO_3,H_2O$; if below 170°, $Bi_2O_3,4SO_3,10H_2O$.

This temperature 170° is that at which the acid sulphates are decomposed when heated in an air-bath, the normal bismuth sulphate, $Bi_2O_3,3SO_3$ being formed.

156. "On sulphates of the form $R_2SO_4,2MSO_4$, especially those of isometric crystallisation." By F. R. Mallet.

During an examination of langbeinite ($K_2SO_4,2MgSO_4$), from the Punjab (*Min. Mag.*, 1899, **12**, 159), the author noticed that the mineral, which fuses at a red heat, on cooling solidifies to a more or less distinctly crystalline mass. This observation naturally suggested that the salt might probably be artificially produced by fusing potassium and magnesium sulphates together in the proper proportions. The crystalline mass obtained on cooling the fused sulphates contains especially in the cavities abundant octahedral crystals sometimes over a millimetre in diameter.

As it seemed probable that other salts of similar constitution might be produced in the same way, the author has prepared the following sulphates of isometric symmetry: $K_2SO_4,2MgSO_4$; $K_2SO_4,2ZnSO_4$; $K_2SO_4,2MnSO_4$; $K_2SO_4,2NiSO_4$; $K_2SO_4,2CoSO_4$; $Rb_2SO_4,2MgSO_4$. Measurements of the angles of the crystals, and partial, or complete, analyses of the above salts are given; their mode of decomposition by absorption of water is also described.

Mixed crystals of isometric symmetry containing more than two of the above metals have also been produced, as well as various anisotropic salts, which have not as yet been examined in detail.

157. "Reactions of the so-called dibenzylamarine." By Francis R. Japp, F.R.S., and James Moir, M.A., B.Sc.

In a recently published note (*Proc.*, 1899, **15**, 211), the authors showed that the compound melting at 139—140°, obtained by Claus and Elbs (*Ber.*, 1880, **13**, 1420) by the action of potassium hydroxide on dibenzylamaronium chloride, and described as dibenzylamarine, is in reality benzoyl-*s*-dibenzyl-*i*-diphenylethylenediamine, $\begin{matrix} C_6H_5\cdot CH\cdot N(C_7H_7)\cdot CO\cdot C_6H_5 \\ C_6H_5\cdot CH\cdot NH\cdot C_7H_7 \end{matrix}$. The following are various experimental results obtained in the study of this substance.

Action of nitrous acid.—This yields, as chief product, a *nitroso*-compound, $C_{21}H_{17}(C_7H_7)_2N_2(NO)O$ (dimorphous: short needles, m. p. 166°; and oblong laminæ, m. p. 168°), together with *dibenzylamaronium nitrate*, $C_{21}H_{17}(C_7H_7)_2N_2\cdot NO_3$, and a little lophine. The second of

these three compounds was also prepared from dibenzylamaronium chloride and silver nitrate, thus proving its constitution. When "dibenzylamarine" nitrate, $C_{21}H_{16}(C_7H_7)_2N_2O,HNO_3$, was heated at 185°, it was converted into a mixture of dibenzylamaronium nitrate and the foregoing nitroso-compound. *Dibenzylamaronium nitrite* (from the quaternary chloride and silver nitrite) is an uncrystallisable gum, quite distinct from the isomeric nitroso-compound.

Reduction with hydriodic acid.—By boiling "dibenzylamarine" with hydriodic acid (sp. gr. 1·7) for some hours, the following products were obtained: as chief product, *benzoylbenzyl-i-diphenylethylenediamine*, $C_6H_5\cdot CH\cdot NH\cdot CO\cdot C_6H_5$ (minute needles, m. p. 218°, basic, and yielding $C_6H_5\cdot CH\cdot NH\cdot C_7H_7$

a *nitroso*-compound, m. p. 246°); *benzyl-i-diphenylethylenediamine*, $C_6H_5\cdot CH\cdot NH_2$ (slender needles, m. p. 90°, converted by benzoic $C_6H_5\cdot CH\cdot NH\cdot C_7H_7$

chloride into the foregoing compound melting at 218°); and, further, dibenzyl, benzylic iodide, benzoic acid, benzylamine, and ammonia.

Action of sodium in boiling alcohol.—An almost quantitative yield of Grossmann's *s*-dibenzyl-*i*-diphenylethylenediamine (*Ber.*, 1889, **22**, 2301) was obtained.

Action of potassium hydroxide.—No action takes place in alcoholic solution at 150°, but on fusing the compound with potassium hydroxide, it yielded the foregoing *s*-dibenzyl-*i*-diphenylethylenediamine, together with benzyllophine and a crystalline, non-basic substance melting at 128°, which gave figures agreeing with the formula $C_{28}H_{24}N_2O$.

Oxidation.—The authors confirmed Claus's observation that "dibenzylamarine" is not altered by boiling with chromium trioxide in glacial acetic acid solution, but found that when a little concentrated hydrochloric acid was added to the mixture, oxidation took place on boiling, and benzoylbenzyl-*i*-diphenylethylenediamine, $C_{28}H_{26}N_2O$ (m. p. 218°)—already obtained in the reduction with hydriodic acid—was formed.

Action of heat.—The chief products were lophine and benzyllophine.

158. "Note on iso-amarine." By H. Lloyd Snape, D.Sc., Ph.D.

As Japp and Moir have recently published (*Proc.*, 1899, **15**, 211) their reasons for regarding the isomeride of amarine described by Brooke and the author (*Trans.*, 1899, **75**, 208) as a racemic form of amarine, the author wishes to report that he has succeeded in separating this isomeride, by means of tartaric acid, into two varieties of equal and opposite optical activity. The author hopes to give a detailed account of these and other experiments on iso-amarine at an early date.

159. "On the preparation of benzene azo-orthonitrophenol." By J. T. Hewitt, M.A., D.Sc.

Noelting (*Ber.*, 1887, **20**, 2997) has observed that the nitration of benzeneazophenol in a strong sulphuric acid solution leads to the formation of paranitrobenzene azophenol, $NO_2 \cdot C_6H_4 \cdot N : N \cdot C_6H_4 \cdot OH$. The author of the present communication finds that by nitrating benzeneazophenol (10 grams) with dilute nitric acid [20 c.c. nitric acid (sp. gr. 1·36) and 60 c.c. water] at 40°, the product of the reaction is benzeneazo-orthonitrophenol, $C_6H_5 \cdot N : N \cdot C_6H_3(NO_2)(OH)$, m. p. 128·5° (corr.). This difference in behaviour can be readily explained since Noelting nitrated a sulphate of benzeneazophenol, which is probably a derivative of quinone phenylhydrazone, $C_6H_5 \cdot NH \cdot N : C_6H_4 : O$, whilst the author of the present paper chose nitric acid of such a dilution as to exclude salt formation and hence nitrated benzeneazophenol, $C_6H_5 \cdot N : N \cdot C_6H_4 \cdot OH$, itself. The result is not compatible with Hantzsch's formulation of the azophenols as quinone-hydrazones when in the free state (*Ber.*, 1899, **32**, 3089), since, whilst phenols are more readily substituted than benzene nuclei not containing hydroxyl or amino-groups, on the other hand amino-derivatives of benzene are certainly more easily substituted than quinones. Certain derivatives of benzeneazo-orthonitrophenol are described in the paper.

160. "Some new osazones and tetrazones." By Harold A. Auden.

None of the three possible isomeric forms of tetrazine (which may be described, according to the relative positions of the ring components, as *v*-, *s*-, or *a*-tetrazines) has yet been isolated. Derivatives of the first of these are represented in the osotetrazones obtained by Pechmann by the oxidation of osazones (*Ber.*, 1888, **21**, 2751). A benzene derivative has also been obtained by Hempel (*J. pr. Chem.*, **41**, 176), and perhaps the substances named diazohydrides by Zincke (*Ber.*, 1886, **19**, 1451; 1888, **21**, 543) belong to this class.

Representatives of *s*-tetrazine have been obtained by Ruhemann (*Trans.*, 1888, **53**, 850; 1889, **55**, 242; 1890, **57**, 50) and Pinner (*Ber.*, 1893, **26**, 2126; 1894, **27**, 984, 3273). Ruhemann (*Trans.*, 1899, **75**, 1131) has obtained a dihydro-derivative of *s*-tetrazine ("tetrazoline") from monoformylhydrazine, and Pellizzari (*Atti R. Acad. Lincei*, [v], 1899, **8**, 327) from diformylhydrazine.

The author has prepared certain osazones and tetrazones with a view to obtaining from them, by a process of oxidation, *v*-tetrazine, $\begin{matrix} H \cdot C : N \cdot N \\ | \quad\quad | \\ H \cdot C : N \cdot N \end{matrix}$. The various stages of the oxidation may probably be represented by the formulæ

$$\begin{matrix} CH_3\cdot C{:}N\cdot NC_6H_4OH \\ \quad\vdots\quad\quad\vdots \\ HC{:}N\cdot NC_6H_4OH \end{matrix} \rightarrow \begin{matrix} CO_2H\cdot C{:}N\cdot N \\ \quad\vdots\quad\quad\| \\ H\cdot C{:}N\cdot N \end{matrix} \rightarrow \begin{matrix} HC{:}N\cdot N \\ \quad\vdots\quad\| \\ HC{:}N\cdot N \end{matrix},$$

similar to those in the cases of osotriazole (*Annalen*, 1891, **262**, 303), tetrazole (*Ber.*, 1895, **28**, 1688), and triazole (*Ber.*, 1885, **18**, 1550, 2907).

The methods which may be used for the preparation of the substances dealt with in the paper are as follows: (1) The action of nitrosoacetone on hydrazines, with the intermediate formation of hydrazoximes. (2) The interaction of diketones and hydrazines. In the former case, it is not necessary to isolate the nitrosoacetone, but by so doing the reaction is more under control and the yield consequently increased by 1 to 2 per cent. In the latter method, the reaction may be thus represented by $\begin{matrix} X-C{:}O \\ \quad\vdots \\ X-C{:}O \end{matrix} + \begin{matrix} H_2N\cdot NH-X \\ \quad\vdots \\ H_2N\cdot NH-X \end{matrix}$, yielding the osazone which, by careful oxidation by means of dilute acetic acid and potassium dichromate or by amyl nitrite, loses two atoms of hydrogen, forming the corresponding tetrazone. The latter method gave better yields, the hydrazoximes frequently decomposing with the production of uninviting, resinous products. In attempting to oxidise the tetrazones, further difficulties have been met with, due partly to their great stability, and partly to the difficulty in some cases of producing the tetrazone from the osazone. The actions of various oxidising agents have been studied, especially those of potassium permanganate in alkaline solution at 80—100°, and of amyl nitrite. It may here be pointed out that oxidation in acid solution is excluded because of the tendency of tetrazones to form triazole derivatives as shown by Pechmann. A mixed osazone was also prepared, as it seemed probable that this might yield a 'tetrazolium' on oxidation similar to the product obtained by Pechmann and Wedekind (*Ber.*, 1894, **27**, 320), and that this in turn might yield further interesting products.

Although the experiments as yet carried out have not led to the isolation of *v*-tetrazine, the following substances have been prepared:

Methylglyoxal-p-*ethoxyphenylhydrazoxime*, $\begin{matrix} CH_3\cdot C{:}N\cdot NHC_6H_4(OEt) \\ \quad\vdots \\ HC{:}N\cdot OH \end{matrix}$, brownish-yellow plates, with golden-yellow reflex, melting at 104—106°, with rapid decomposition. It can be recrystallised from methyl alcohol, but in solution is unstable.

Methylglyoxal-p-*ethoxyphenylosazone*, $\begin{matrix} CH_3C{:}N\cdot NHC_6H_4(OEt) \\ \quad\vdots \\ HC{:}N\cdot NHC_6H_4(OEt) \end{matrix}$, reddish-yellow needles, m. p. 135°. With strong sulphuric acid, it gives deep-green solution.

Methylglyoxal-p-ethoxyphenylosotetrazone, $\begin{matrix}CH_3\cdot C:N\cdot N\cdot C_6H_4(OEt)\\ |\\ HC:N\cdot N\cdot C_6H_4(OEt)'\end{matrix}$ crystallises in Bordeaux-red needles, which cannot be distinguished in shade from those of methylglyoxalosotetrazone. It dissolves in strong hydrochloric acid with indigo-blue coloration, which disappears on heating; with strong sulphuric acid it gives a similar coloration, rapidly becoming green. It is not attacked by alkaline potassium permanganate in the cold, and only with difficulty at 100°.

Diazosalicylic acid, $C_6H_3\begin{matrix}OH\ (2)\\ COO\ (1)\\ N:N\ (5)\end{matrix}$ and $C_6H_3\begin{matrix}OH\\ CO_2H\\ N:N\cdot Cl\end{matrix}$. The former explodes at 155°, the latter about the same temperature, decomposition generally beginning about 10° lower. The chloride loses hydrogen chloride in the desiccator over soda and when exposed to the air. The free diazo-compound varies in shade from yellow to greenish-yellow; the chloride forms nearly colourless needles. If only gently heated, both may be recrystallised from water.

Potassium diazosalicylic acid sulphonate, $C_6H_3(OH)COOK\cdot N:NSO_3K$, is a fairly stable compound which may be recrystallised from water, and dried at 100°. It crystallises in yellow plates.

Hydrazine salicylic acid, $C_6H_3\begin{matrix}CO_2H\ (1)\\ OH\ (2)\\ NH\cdot NH_2\ (5)\end{matrix}$. This is a slightly brown amorphous powder which melts at 148°. The hydrochloride crystallises in snowy needles which char at 150°. It reduces Fehling's solution slowly in the cold and gives a white, crystalline hydrazone with benzaldehyde.

Methylglyoxal-salicylic acid osazone, $\begin{matrix}CH_3\cdot C:N\cdot NHC_6H_3(OH)(COOH)\\ |\\ HC:N\cdot NHC_6H_3(OH)(COOH)'\end{matrix}$ a bright yellow, crystalline powder, m. p. 192°. It gives a dark green coloration with ferric chloride. The corresponding hydrazoxime could not be isolated, and probably does not exist, as on using only one molecule of hydrazine the osazone was formed.

Acetyl-propionylsalicylic acid osazone, $\begin{matrix}CH_3\cdot C:N\cdot NHC_6H_3(OH)(COOH)\\ |\\ C_2H_5C:N\cdot NHC_6H_3(OH)(COOH)'\end{matrix}$ may be obtained in very small, yellow crystals by adding water to its solution in alcohol.

On boiling the crude product with alcohol, a yellow residue was invariably left; this residue melted at 220°, but yielded the same numbers on analysis as the more soluble portion which melted at 197°, and is possibly a stereoisomeride. This substance is apparently attacked by oxidising agents, but it does not give the osazone reaction. It yielded, on oxidation with potassium permanganate or

potassium ferricyanide, small amounts of a white, crystalline substance which gave a characteristic wine red coloration with ferric chloride.

Methylglyoxal-methylphenyl-phenylosazone, $CH_3 \cdot C(:N \cdot NHC_6H_5) \cdot N(CH_3)(C_6H_5)$, yellow needles (m. p. 119—120°) slightly darker in shade than methylglyoxal-phenylosazone, gives a deep red coloration with strong sulphuric acid.

The author is led to publish this preliminary note now, as owing to a loss through fire of notes and products, some months must elapse before the results of the oxidation experiments can be published in detail.

161. "A series of substituted nitrogen chlorides. Part II. The trichloro-phenyl-acyl-nitrogen chlorides." By F. D. Chattaway and K. J. P. Orton.

This paper is a continuation and completion of the authors' previous work on the substituted nitrogen chlorides which are directly obtainable from formanilide, acetanilide, and benzanilide.

It is shown that in anilides the formation of a nitrogen chloride or bromide in all cases precedes substitution in the nucleus and that the degree of difficulty with which the transformation of these nitrogen chlorides and bromides can be effected corresponds with the relative difficulty of obtaining the transformation products directly by the action of the halogen.

The following compounds are described.

2:4:6-*Trichloro-phenyl-formyl nitrogen chloride*, $C_6H_2Cl_3 \cdot NCl \cdot CHO$, brilliant white prisms terminated by domes, m. p. 78°; 2:4:6-*Trichloro-phenyl-acetyl nitrogen chloride*, $C_6H_2Cl_3 \cdot NCl \cdot COCH_3$, white, transparent, prismatic crystals resembling cubes, m. p. 74°; 2:4:6-*trichloro-phenyl-benzoyl nitrogen chloride*, $C_6H_2Cl_3 \cdot NCl \cdot COC_6H_5$, thick white prisms terminated by pyramids, m. p. 89°; p-*chloro-phenyl-benzoyl nitrogen chloride*, $C_6H_4Cl \cdot NCl \cdot COC_6H_5$, glistening short white prisms with domed ends, m. p. 79·5°.

These compounds all show the general reactions characteristic of the nitrogen halogen linkage.

162. "The reaction between cupric sulphate solution and magnesium, zinc, and iron." By R. M. Caven, B.Sc., F.I.C.

When magnesium, zinc, or iron reacts with cupric sulphate solution, the usual assumption of simple replacement of metal by metal is in

no case found to be exactly true; cuprous oxide invariably occurs to a greater or less extent together with metallic copper in the residue.

The suggestion of Divers (*Proc.*, 1898, 14, 57) that the cuprous oxide formed in the reaction with magnesium is due to the production of cuprous sulphate, is well in accord with the facts established; but the separation of cuprous oxide is not connected with the formation of the basic cupric sulphate produced by hydrolysis, as suggested by Divers, since it is produced in considerable quantity, together with an equivalent amount of sulphuric acid, in hot strong solutions, in which spontaneous hydrolysis of cupric sulphate with separation of insoluble basic salt does not occur. That the cuprous oxide is produced by the hydrolysis of cuprous sulphate is borne out by all the facts; and this view is supported by the observations of F. Foerster (*Zeit. Elektrochemie*, 1897, 3, 479, 493).

In all the reactions examined, with the exception of that of iron reacting with cold solutions, hydrogen is evolved, though sometimes in small quantity only. J. B. Senderens states that hydrogen is evolved in this case also (*Bull. Soc. Chim.*, 1897, [iii], 17, 271), though his statement is not confirmed by the experiments of the author.

In those cases in which only copper and cuprous oxide appeared in the residue, the hydrogen evolved was calculated from the deficiency of the acid remaining in the solution from the quantity equivalent to the cuprous oxide found. This agreed with actual measurement; and also the sum of the equivalents of the copper, cuprous oxide, and hydrogen thus calculated, was equal to the quantity of the displacing metal employed.

The evolution of hydrogen in each case is due to one or more of the following distinct causes:

I. Reaction of displacing metal with sulphuric acid produced

(*a*) By hydrolysis of cupric sulphate, resulting in separation of insoluble basic cupric salt (Divers).

(*b*) By hydrolysis of cuprous sulphate, resulting in separation of cuprous oxide.

II. Action of the metallic couple upon the water of the solution.

III. Very slight reaction of finely-divided precipitated copper, with hot, dilute sulphuric acid, produced according to I (*b*).

In all cases except that of magnesium reacting with dilute solution, in which case the permanent separation of basic compounds takes place, the evolution of hydrogen may be eventually referred to the acid produced by hydrolysis of cuprous sulphate only.

The production of cuprous oxide and sulphuric acid in appreciable amount and in equivalent quantities, when cupric sulphate solution is brought into contact with finely-divided copper under various conditions, shows that cuprous sulphate is produced synthetically in the

above reactions. It is, however, believed that in most cases cuprous sulphate is also formed by the reduction of cupric sulphate by the replacing metal.

ADDITIONS TO THE LIBRARY.

Donations.

Landolt, H. Optical activity and chemical composition. Translated by John McCrae. London 1899. From the Publishers.

Walker, James. Introduction to physical chemistry. London 1899. From the Author.

Lehfeldt, R. A. A text-book of physical chemistry. London 1899. From the Publishers.

Collins, S. H. Handbook of agricultural chemistry for Indian students. Calcutta 1898. From the Author.

Cooper, A. J. Elementary practical chemistry. London 1899. From the Publishers.

Schuyten, M. C. Beginselen der scheikunde. Antwerpen 1899. From the Author.

Roscoe, Sir Henry, and Harden, Arthur. Inorganic chemistry for advanced students: ill. London 1899. From the Authors.

At the next meeting, on Thursday, December 21st, the following papers will be communicated:—

"The condensation of glycollic aldehyde and formation of α- and β-acrose." By Henry Jackson, B.A.

"On brasilin and hæmatoxylin. Part III." By A. W. Gilbody and W. H. Perkin, jun.

"The action of alcoholic potash on monobromoglutaric ester." By N. E. Bowtell and W. H. Perkin, jun.

"Mercurous iodide." By P. C. Rây, D.Sc.

"On the interaction of mercurous nitrite and ethyl iodide." By P. C. Rây, D.Sc.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

Vol. 15. No. 216.

December 21st, 1899. Professor Thorpe, F.R.S., President, in the Chair.

Dr. Kohn was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Granville Reginald Gee, Falcon Villa, Howard Street, Gloucester; Alfred William Harvey, 13 Pendrell Road, St. Catherine's Park, Hatcham, S.E.; Thomas Ebenezer Mackenzie, 6 Cardonald Terrace, Cardonald, near Glasgow; William Mair, 388 Morningside Road, Edinburgh; John Livingston Rutgers Morgan, 47 Bayard Street, New Brunswick, New Jersey, U.S.A.; James Fraser Readman, 50 Jane Street, Glasgow; James McConnell Sanders, 37 Summerhill Road, Dartford; and of Sidney Calvert, Missouri State University, Columbia, Missouri, whose Certificate was approved by Council under Bye-law I (3).

The SECRETARY read the following letter, written by the President at the request of the Council, to Professor Emil Fischer, a Foreign Member of the Society, congratulating him on the completion of the twenty-fifth year of his Doctorate, together with a translation of Professor Fischer's reply.

16*th November*, 1899.

MY DEAR COLLEAGUE,

As President of the Chemical Society, I have the pleasure to offer you, by request of the Council, the warmest congratulations of the Fellows on the completion of the twenty-fifth year of your Doctorate.

It is not often that so short a span of intellectual activity in the life of any one individual comprehends such a brilliant series of scientific triumphs as those with which you have enriched chemistry.

That you may long be spared to cultivate the many fields of fruitful inquiry you have so assiduously opened up is the fervent wish of this Society, which recalls with pride that it numbers you amongst the most distinguished of its Foreign Members.

I have the honour to be, with great respect,

My dear Colleague,

Your obedient humble Servant,

T. E. THORPE,
President.

To Professor Dr. EMIL FISCHER,
Berlin.

The following is the translation of Professor Fischer's reply:—

10, DOROTHEENSTRASSE,
BERLIN.
29th *November*, 1899.

HIGHLY ESTEEMED PRESIDENT,

I have been most agreeably surprised by the honour as well as the heartiness of the congratulations which you have conveyed to me in the name of the Chemical Society on the occasion of the celebration of the 25th year of my Doctorate. Your Society and other learned bodies in England have indeed done me so much honour that I am obliged to ask myself, with diffidence, whether it bears any relation to my achievements.

The time when the fundamental principles of our Science were laid down, and when it was possible for the individual investigator to stamp the impress of his own mind upon it, is long since past, and in the gigantic structure which it now represents, each fellow-worker can only finish some small fragment, or it may be, if he is fortunate, a pretty balcony or a striking turret. The progress of the whole, is however, most readily accomplished by the combined efforts of numerous gifted and skilled observers. This co-operation, so characteristic of the scientific work of the present day, is exhibited in its highest form by the great Chemical Societies, of which yours is the oldest and has served as a model for the others.

I am proud, therefore, to be allowed to belong to it as a Foreign Member, and I beg, esteemed President, that you will be so good as to

convey to your Council my heartfelt thanks for their kind congratulations.

With the highest esteem,

Yours obediently,

EMIL FISCHER.

PROF. DR. THORPE,
President of the Chemical Society,
London.

Of the following papers, those marked * were read.

***163. "On the refractive and magnetic rotatory powers of some aromatic hydrocarbons, and on the refractive powers of mixtures." By W. H. Perkin, LL.D., F.R.S.**

The first part of the paper deals with a comparison of the magnetic rotatory and refractive powers of aromatic hydrocarbons undertaken to see if these properties were analogous in character. Most of the hydrocarbons employed were of exceptional purity, many being prepared from the pure salts of their sulphonic acids. An account is given of the preparation and properties of *isobutylbenzene*, prepared by this method for the first time.

With regard to the refractive powers of these substances, the results obtained show that the replacement by methyl of a hydrogen atom in the nucleus gives a value considerably *larger* than when the replacement takes place outside, and this is so certainly up to four such replacements, and therefore probably for the six. The replacement of hydrogen outside the nucleus by methyl (as in the conversion of toluene into ethylbenzene) also gives results somewhat higher than those calculated, but these values tend to coincide more nearly as the distance from the nucleus increases.

With the magnetic rotations, the reverse was found to hold, as a considerably *smaller* increase in the rotation is produced by a change in composition of CH_2 in the nucleus, than when it occurs outside. This holds for four replacements, and therefore probably for all.

These results are remarkable when the general correspondence between the magnetic rotatory and refractive powers of compounds is considered.

The second part refers to the refractive powers of mixtures. It has been shown that in the case of the magnetic rotations of mixtures these are usually less than those calculated from the molecular rotations of the constituents when their specific rotations are widely apart, hence it was of interest to determine whether a similar differ-

ence existed in the case of the refractive powers of mixtures. It was found that when the two constituents had very widely differing indices of refraction the specific, or molecular refraction was considerably lower than that calculated, but that when indices were nearly the same, the calculated and observed values agreed very well. That this latter statement holds, was shown by means of a mixture (*a*) of fatty compounds, (*b*) of aromatic compounds. These differences were most marked in mixtures of two fatty compounds having indices widely apart; in mixtures of a fatty with an aromatic compound, they were less pronounced.

Many of Zecchini's experiments with mixtures give results of a similar character to those described above, but exceptions occur which seem to indicate that although the differences between the refractive powers of the substances employed appear to be the chief cause of these peculiar results, other causes must also be at work. A new and improved arrangement for reading the scale and vernier of the spectrometer was described and shown.

Discussion.

The President, after recalling the fact that differences similar to those observed by the author had been also observed with regard to the viscosity of pure compounds and mixtures of them, inquired why mixtures in equal volumes rather than in molecular proportions had been employed in this investigation.

Dr. Gladstone remarked that the results of the author to a certain extent explained some of the difficulties met with by early workers in the field of molecular refraction, and that many of them had observed similar small differences which were yet quite beyond the limit of experimental error. There was no doubt that researches such as those of Dr. Perkin must tend to throw more and more light on the causes of these small divergences in the optical properties and hence to reveal more fully the structure of the molecule.

Dr. Perkin, in reply, said that the use of mixtures of equal volumes of the constituents had originated in his work on magnetic rotation, as such mixtures allowed of more ready comparison of the indices of refraction, densities, &c., of the mixtures and their components.

*164. "Formation of α- and β-acrose from glycollic aldehyde." By Henry Jackson, B.A.

When a dilute (3 per cent.) aqueous solution of glycollic aldehyde is allowed to stand with a 1 per cent. solution of soda for 15 hours at 0°,

it is still able to reduce Fehling's solution in the cold (though not so strongly as a solution of glycollic aldehyde), and to restore the colour to an alcoholic solution of magenta which has been decolorised by sulphurous acid. If the condensation product be neutralised with acetic acid, then heated on the water-bath with phenylhydrazine acetate, an osazone is obtained which, on purification and fractional treatment with various solvents, can be shown to contain tetrosazone [obtained previously by Fischer and Landsteiner, (*Ber.*, 1892, 25, 2549), by condensing glycollic aldehyde with soda at 0°], and two hexosazones, α-acrosazone, m. p. 217°, and β-acrosazone, m. p. 158°.

If the condensation be allowed to proceed for a longer time at 0°, it is found that the power of reducing Fehling's solution in the cold gradually diminishes until, after standing 6 days, it no longer reduces in the cold, but quickly on warming. The osazone obtained consists almost entirely of a mixture of the two hexosazones (α- and β-acrosazone), only a trace of tetrosazone being found.

Discussion.

Mr. Fenton said that it was evident, both from these and from previous observations, that the condensation products of glycollic aldehyde and of formaldehyde were identical. It was probable that glycollic aldehyde was an intermediate stage in the condensation of formaldehyde, especially as Pechmann (*Ber.*, 1897, 30, 2459) had shown that the osazone of glycollic aldehyde could be obtained directly from formaldehyde and phenylhydrazine in acetaldehyde solution.

165. "The interaction of mercurous nitrite and ethyl iodide." By P. C. Rây, D.Sc.

When mercurous nitrite acts upon ethyl iodide, about equal quantities of nitroethane and its isomeride, ethyl nitrite, are formed. The yield is, however, somewhat poorer than when silver nitrite is used, owing to the formation of very compact lumps of mercurous iodide, which prevents the reaction from becoming complete.

166. "On mercurous iodide." By P. C. Rây, D.Sc.

When the residue in the flask after the interaction of mercurous nitrite and ethyl iodide is heated in a tube, mercurous iodide sublimes off between 190° and 210°. The compact mass of crystalline tablets thus obtained shows all gradations of tint from lemon- and orange-yellow to dark brown.

167. "The action of alkyl iodides on the mercuric iodide sulphides of the fatty series." By Samuel Smiles, B.Sc.

The alkyl sulphides unite with mercuric iodide to form compounds of the general formula R_2SHgI_2. Like other addition products of the sulphides, their constitution should be represented as $\begin{matrix}R\\R\end{matrix}\!>\!S\!<\!\begin{matrix}HgI\\I\end{matrix}$.

The following members of the series were examined:

Me_2SHgI_2, long, yellow needles from acetone, m. p. 75°.

$MeEtSHgI_2$, short prisms from acetone, m. p. 59°.

Et_2SHgI_2, yellow prisms from acetone, m. p. 52°.

$(C_5H_{11})_2SHgI_2$ (isoamyl), yellow oil.

$(C_7H_7)_2SHgI_2$, pale yellow plates from acetone, m. p. 37—38°.

These substances are unstable, readily splitting off mercuric iodide when exposed for any length of time to the air, or when boiled with water. Dimethylsulphide mercuric iodide, when treated with methyl iodide, yields the same product as that obtained from trimethylsulphine iodide and mercuric iodide, namely, Me_3SIHgI_2. The same holds good for the triethyl derivative. Hence the double salts formed from mercuric iodide and sulphine iodide appear to contain hexavalent sulphur, as their constitution may be represented as $R_3{:}S\!<\!\begin{matrix}I_2\\HgI\end{matrix}$. Therefore, it was hoped that an investigation of the derivatives containing different alkyl groups would yield evidence as to the stereochemical nature of hexavalent sulphur. So far, however, only negative results have been obtained.

The following substances were prepared and examined:

Me_3SI_2HgI, large, yellow prisms from acetone, m. p. 165°.

From (1) Me_3SI and HgI_2; (2) Me_2SHgI_2 and MeI.

Me_2EtSI_2HgI, long, yellow prisms from acetone, m. p. 87°.

From (1) Me_2EtSI and HgI_2; (2) Me_2SHgI_2 and EtI; (3) $MeEtSHgI_2$ and MeI.

$MeEt_2SI_2HgI$, bright yellow prisms from acetone, m. p. 67°.

From (1) Et_2MeSI and HgI_2; (2) Et_2SHgI_2 and MeI; (3) $MeEtSHgI_2$ and EtI.

Et_3SIHgI_2, bright yellow leaflets from acetone, m. p. 112°.

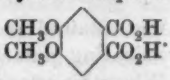
From (1) Et_3SI and HgI_2; (2) Et_2SHgI_2 and EtI.

Just as in the case of the nitrogen compounds such isomerism as might be expected here may be prevented by the presence of methyl or ethyl groups, it will therefore be necessary to repeat this with derivatives containing more complex radicles.

Attempts were also made to resolve methyl ethyl thetine, $MeEtS\!<\!\begin{matrix}CH_2\cdot CO\\O\end{matrix}$, into optically active components, but without success.

168. "On brasilin and hæmatoxylin. Part III." By A. W. Gilbody and W. H. Perkin, jun.

In a previous communication (*Proc.*, 1899, **15**, 27), an acid obtained from brasilin was described which melted at 155° and gave, on analysis, numbers agreeing with the formula $C_{15}H_{16}O_6$. This acid, on oxidation with potassium permanganate, yielded a dibasic acid melting at 200—203°, which, when heated with hydrochloric acid at 160°, was decomposed with formation of catechol. Further investigation has shown that this acid, which at first was thought to have the formula $C_{10}H_{10}O_3(CO_2H)_2$, is in reality *metahemipinic acid*,



This has been conclusively proved by converting the acid into its anhydride and characteristic ethylimide (m. p. 230°). *Tetramethylhæmatoxylin*, when oxidised with chromic acid, also yields considerable quantities of *metahemipinic acid*, a proof that hæmatoxylin, like brasilin, is a derivative of catechol. As this result does not agree with the statement of R. Meyer (*Ber.*, 1879, **12**, 1393) that hæmatoxylin, on distillation, yields pyrogallol and resorcinol, we have repeated this work, and find that the products of the destructive distillation of hæmatoxylin contain considerable quantities of pyrogallol, but, as far as we could determine, no trace of resorcinol.

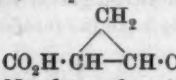
It follows, therefore, from these experiments, that whereas brasilin is a derivative of resorcinol and catechol, hæmatoxylin is a derivative of pyrogallol and catechol.

The formation of metahemipinic acid from both brasilin and hæmatoxylin shows that the formulæ which we suggested for these substances require some modification. It would be easy to construct formulæ which would take these new facts into account, but we prefer to wait until further experimental evidence is forthcoming before doing so. We hope, therefore, that others working in this field will allow us to reserve for a short time the deduction of any formulæ for brasilin and hæmatoxylin which are based on the new results described in this and the two preceding preliminary communications.

It should be noticed that the melting point of tetramethylhæmatoxylone is incorrectly given as 170° in the previous communication, it should be 183—186° with vigorous decomposition.

169. "The action of alcoholic potash on monobromoglutaric ester." By N. E. Bowtell and W. H. Perkin, jun.

A short time since (*Trans.*, 1899, **75**, 50) it was shown by J. F. Thorpe and one of us that when *monobromodimethylglutaric ester*,

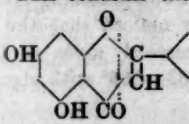
$CO_2Et\cdot CHBr\cdot CMe_2\cdot CH_2\cdot CO_2Et$, is digested with alcoholic potash, it yields a mixture of *cis*- and *trans*-dimethyltrimethylenedicarboxylic acids (caronic acids), It occurred to us that it would be interesting to investigate the behaviour of *monobromoglutaric ester*, $CO_2Et\cdot CHBr\cdot CH_2\cdot CH_2\cdot CO_2Et$, under similar conditions, as in this case there are two possibilities, namely, either glutaconic acid, $CO_2H\cdot CH{:}CH\cdot CH_2\cdot CO_2H$, or trimethylenedicarboxylic acid,  , could be formed.

Monobromoglutaric ester was obtained as a colourless oil boiling at 165—170° (35 mm.) by brominating glutaric anhydride and pouring the product into alcohol. When this ester is decomposed by alcoholic potash, an acid is obtained melting at 175°, which on examination was found to consist of trans-*trimethylenedicarboxylic acid*, and we were unable to isolate even traces of glutaconic acid.

This remarkable result points to the possibility that many substances produced by similar reactions and described as unsaturated may in reality be derivatives of trimethylene, tetramethylene, &c.

We are engaged in investigating the action of alcoholic potash on the esters of bromine substitution products of adipic, pimelic, and allied acids.

170. "Luteolin. III." By A. G. Perkin.

Previous investigations (*Trans.*, 1896, **69**, 206, 799) indicated that luteolin, $C_{15}H_{10}O_6$, is a tetrahydroxyflavone. The energetic action of alkali yielded phloroglucinol and protocatechuic acid, confirming Rochleder's results (*Zeit. für Chem.*, 1866, **2**, 602), and it is now found that, by gentler treatment, phloroglucinol and a substance having the composition $C_8H_8O_3$ are formed. ($C = 63{\cdot}16$; $H = 5{\cdot}26$. Found $C = 63{\cdot}47$; $H = 5{\cdot}61$). The substance (colourless needles, m. p. 115—116°) gives, with fused alkali, protocatechuic acid, and its properties are identical with those of *acetylcatechol*, $CH_3\cdot CO\cdot C_6H_3(OH)_2$ (Dzerzgowski, *Journ. Russ. Chem. Soc.*, 1893, **25**, 157). This confirms the constitution assigned by the author to luteolin,  , and is identical in its nature with the decompositions of chrysin, $C_{15}H_{10}O_4$ (Kostanecki, *Ber.*, 1893, **26**, 2901), and apigenin (*Trans.*, 1897, **71**, 805), which respectively yield phloroglucinol and acetophenone, and phloroglucinol and *p*-hydroxyacetophenone.

In conjunction with Mr. L. H. Horsfall, an investigation is in progress upon certain ethers of luteolin. By partial methylation, a *dimethyl ether* (found C = 65·06; H = 4·55; CH_3 = 9·92), colourless needles, m. p. 227—229°, is formed in small quantity; this is almost devoid of dyeing property, and by means of alkali gives *isovanillic acid*. There is evidence that, in addition to luteolin, weld contains a trace of a second colouring matter.

171. "The action of chloroform and potassium hydroxide on orthoamidobenzoic acid." By Walter J. Elliott, M.A.

By acting on orthoamidobenzoic acid with chloroform and potassium hydroxide, acidifying the product with acetic acid, and treatment with phenylhydrazine and semicarbazide respectively, the author has obtained the phenylhydrazone and semicarbazone of an aldehydo-orthoamidobenzoic acid. Owing to its great solubility in water, he has failed to obtain the free aldehydo-acid in a state of purity. The barium and silver salts of the phenylhydrazone have been prepared and analysed. The hydrazone and semicarbazone are both very stable.

172. "Azo- and hydrazone compounds differentiated by bromine." By H. E. Armstrong.

Although the constitution of the "oxyazo"-compounds has been the subject of numerous investigations, apparently chemists are not yet in agreement as to their formulæ; indeed, only recently, Hantzsch in Germany, and MacPherson in America, have arrived at diametrically opposite conclusions. The difficulty arises from the fact that para-hydroxyazobenzene—the parent of all "oxyazo"-compounds—and quinonephenylhydrazone are unquestionably isodynamic. Methods such as Hantzsch and Farmer have adopted must, therefore, be regarded as in principle the only suitable ones for the determination of structure in such cases, and extreme care must be taken in interpreting interactions.

A number of observations made in the author's laboratory by Messrs. Panisset, Seligmann, and Isherwood are of interest as bearing on the problem.

The stability of diazobenzene in presence of bromine was established by Griess in his earliest investigation. Diazobenzeneparasulphonate is also untouched by bromine, and action only takes place gradually as it becomes hydrolysed. Azobenzene is only very slowly and imperfectly acted on by bromine. Nitrogen, in fact, by no means tends to promote substitution, unless associated with hydrogen.

If oxyazobenzene were parahydroxyazobenzene, one would expect it to be readily brominated in the ortho-position relatively to the hydroxyl; but, as a matter of fact, it yields a product convertible into parabromaniline and phenol on reduction, and which is easily prepared from these, a result only compatible with the view that towards bromine it behaves as a hydrazone.

This view is confirmed by the fact that when the ethylated compound is brominated, a substance is formed which Mr. Isherwood finds to be identical with that produced on coupling orthobromophenol with diazobenzene and then ethylating. It is noteworthy that the bromine is removed from this compound with exceptional facility, both when dissolved in acetone, and when left in contact with sulphurous acid.

The behaviour of bromine in excess towards the quinhydrazones is characteristic. Quinonebromophenylhydrazone is resolved by it into bromodiazobenzene and tribromophenol, and ordinary tropæolin into diazobenzenesulphonate and tribromophenol. So complete is the change in this latter case, that if, after the tribromophenol has been filtered off, phenol be added to the solution, and then alkali, an amount of tropæolin can be recovered almost equal to that originally taken.

ADDITIONS TO THE LIBRARY.

I. Donations.

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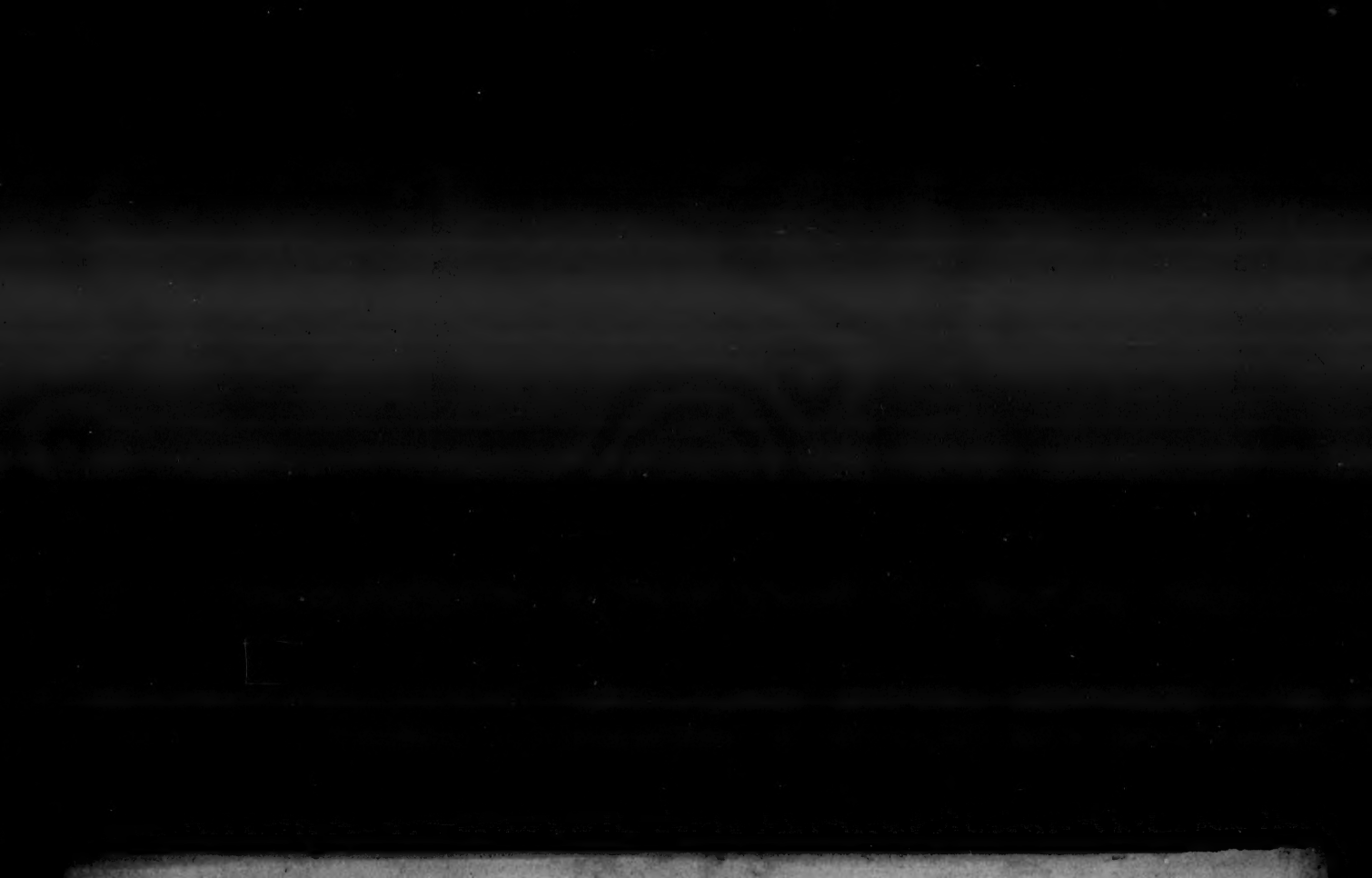
VICTOR MEYER MEMORIAL LECTURE.

The Victor Meyer Memorial Lecture will be delivered by Professor T. E. Thorpe, President of the Society, on the evening of Thursday, February 8th, 1900, at 8.30.

At the next meeting, on Thursday, January 18th, 1900, the following papers will be communicated:—

"Nitrogen halogen compounds." By Julius Steiglitz and E. E. Slosson.

"Chlorine derivatives of pyridine. Part V. Synthesis of $\alpha\alpha'$-dichloropyridine. Constitution of citrazinic acid." By W. J. Sell, M.A., F.I.C., and F. W. Dootson, M.A.

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